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CANADIAN THESES ON MICROFICHE
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NAME OF AUTHOR/*NOM DE L'AUTEUR* PERVAIZ NASIR

TITLE OF THESIS/*TITRE DE LA THÈSE* SOLUBILITY OF CO_2 AND H_2S IN ETHANOLAMINE SOLUTIONS

UNIVERSITY/*UNIVERSITÉ* UNIVERSITY OF ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED/ *GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE* M.Sc

YEAR THIS DEGREE CONFERRED/*ANNÉE D'OBTENTION DE CE GRADE* 1975

NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* DR. A.E. MATHER

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Houston, Texas 77001, USA

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THE UNIVERSITY OF ALBERTA

SOLUBILITY OF CO_2 AND H_2S IN ETHANOLAMINE SOLUTIONS

by

Ⓒ PERVAIZ NASIR

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

IN

CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING
EDMONTON, Alberta
FALL, 1975

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled " SOLUBILITY OF CO_2 AND H_2S IN ETHANOLAMINE SOLUTIONS", submitted by Pervaiz Nasir in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

A E Mather
Supervisor

....

Frank D. Otto

Date 30 July 1975

ABSTRACT

An experimental apparatus was designed, constructed and tested for the measurement of very low partial pressures of H_2S and CO_2 in aqueous ethanolamine (EA) solutions at high temperatures.

The apparatus was tested by measurements of CO_2 and H_2S solubility in the region where previous data were available. Tests were carried out for CO_2 at 60°, 80° and 100°C and monoethanolamine (MEA) concentrations of 2.5 and 5.0 normal (N). For H_2S measurements were made at 80° and 100°C with MEA concentrations of 2.5 and 5.0 N. Good agreement with the literature proved the reliability of the apparatus.

Measurements were also made at conditions where no previous data were available. The 80° and 100°C isotherms, for both pure CO_2 and H_2S in 2.5 N MEA, were extended to very low partial pressure of the acid gas (about 0.0001 psia). Measurements for mixtures of H_2S and CO_2 in 5N MEA at 100°C were also made for very low loadings of CO_2 and H_2S (each being less than about 0.1 mole/mole of MEA) in the liquid phase.

The theoretical models proposed by Klyamer et al.[13] and Kent and Eisenberg[10] were used to predict partial pressures of CO_2 and H_2S. Modifications were carried out in the model of Klyamer et al. by incorporating fugacities of CO_2 and H_2S. The functions, for activity coefficients of

ions in the solution, were modified to include the effects of temperature and initial EA concentrations. Predictions from these three models (namely Klyamer et al., Kent and Eisenberg, and modified Klyamer et al.) were compared with the experimental data obtained in this work, as well as that from the literature. For most cases the Modified Klyamer et al. model gives the best fit of the experimental data. For the simple systems (i.e., aqueous EA solutions containing either CO_2 or H_2S), however, the model of Kent and Eisenberg gives a slightly better fit of the experimental data.

ACKNOWLEDGEMENTS

Sincere thanks are expressed to Dr. Alan E. Mather for his guidance and supervision without which this work would not have been possible.

Helpful criticism and suggestions of fellow graduate students and friends, in particular Jong Il Lee, Jamal Abou-Kassem and Dr. Eddy Isaacs, are gratefully acknowledged. Finally, special thanks are due to the workshop staff for their help in the fabrication of the experimental apparatus.

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NOMENCLATURE

α	Ratio between the un-ionized ethanolamine activity and the activity of water
a	Constant in Redlich-Kwong equation
b	Constant in Redlich-Kwong equation
f	Fugacity
H	Inverse of Henry's Law constant
K	Equilibrium constant
k_{ij}	Characteristic constant for i-j interaction
m	Molality of ethanolamine in Klyamer et al. correlation; molarity of ethanolamine in Kent and Eisenberg correlation
N	Normality of ethanolamine
P_c	Critical pressure
P_{CO_2}	CO_2 partial pressure
P_{H_2S}	H_2S partial pressure
R	Gas constant
T	Temperature
T_c	Critical temperature
v	Molar volume
V_c	Critical volume
X_{CO_2}	Moles of CO_2/mole of ethanolamine
X_{H_2S}	Moles of H_2S.mole of ethanolamine

Y_i	Mole fraction of component i
z	Compressibility factor; carbamate ion concentration
z_c	Critical compressibility factor
Z_i	Electrical charge on an ion

Greek

α	Activity coefficient of water
γ	Activity coefficient of an ion
μ	Ionic strength
ϕ	Fugacity coefficient
Ω	Dimensionless constant in Redlich-Kwong equation
ω	Acentric factor

INTRODUCTION

Aqueous ethanolamines are widely used in industry for removing H_2S and CO_2 from gas streams. Vapor-liquid equilibrium solubility data for H_2S and CO_2 and their mixtures in EA solutions are needed to aid in the design of amine-type natural gas sweetening units. Data of this type allow the estimation of the equilibrium capacity of the amine solution for each different sweetening system design for the particular conditions of temperature, pressure, and concentration found in the processing units. The data may be used to check the feasibility of more economical designs not yet tested by plant experience and, therefore, provide a means to guide a program intended to reduce sweetening plant investment and operating costs.

Solubility data for acid gas-aqueous EA systems have been collected by numerous investigators over the last forty years. However, the data published to date do not cover all the necessary ranges of solution strengths and temperatures. The region of low loadings, in terms of moles of acid gas/mole of EA and low acid gas partial pressure (where most commercial units operate), has not been sufficiently covered. This project was undertaken to cover this important region of very low partial pressures of acid gases and high temperatures. To make these measurements a low pressure apparatus had to be designed and constructed.

To be able to use this apparatus with confidence for regions where no data exist, some measurements had to be made to reproduce existing data.

While the equilibrium solubility data are useful in themselves, it is desirable to have a computer-oriented correlation which reproduces the experimental results, and which can be extrapolated outside the range of the data with some degree of confidence. So far only two solubility models have been proposed for CO_2-H_2S-water-EA systems by Klyamer et al.[13] and Kent and Eisenberg[10]. The starting point for both of these models is the postulation of chemical reactions occuring in the aqueous EA solution containing the acid gases. The model of Klyamer et al. uses activity coefficients, for ions in the solution, to account for the non-ideality of the liquid phase. Kent and Eisenberg have incorporated all the non-idealities in two empirical parameters. They determined these parameters from experimental data. Neither of these models is reliable over all conditions of solution strengths and temperatures. Modifications in the Klyamer et al. model (made in this work) improved substantially, the reliability of prediction of equilibrium partial pressures from a knowledge of liquid composition and temperature.

In Chapter I, design considerations, construction, and operating details of the experimental apparatus are described. In Chapter II, comparison of the experimental data with those of literature is presented in graphical form, along with the data obtained in this work for regions where no previous data are available. Chapter III, discusses the theoretical models for prediction of equilibrium partial pressures of CO_2 and H_2S when other conditions are known. This is followed by comparison of the models.

CHAPTER I

EXPERIMENTAL METHOD

In this chapter the design considerations, construction and operation of the experimental apparatus used in this work will be described.

A. Design Considerations:

Basically three different methods have been employed for vapor liquid equilibrium studies of Hydrogen Sulphide - Carbon Dioxide - Water - Ethanolamine systems:

(a) Static Method
(b) Dynamic Method
(c) Circulation Method

a) Static Method:

In this method a closed cell containing the amine solution with a certain concentration of acid gas (or gases) is used. A motor and gear train usually constitutes the rocking mechanism. The whole assembly is immersed in an oil or air bath. This method has been used by Reed and Wood[28] for measurement of CO_2 partial pressures ranging from 1.5 to 1.7 atm; Jones et.al[9] from 0.56 to 7000 mm of mercury; Goldman and Leibush[8] from 10 to 2000 mm of mercury; Lee, Otto and Mather[15,16] for partial pressures of CO_2

between 0.1 psia and 827 psia and partial pressures of H_2S between 0.1 psia and 306 psia.

b) Dynamic Method:

Either a gas blend of N_2, CO_2 and H_2S or pure N_2 is passed through a number of saturators containing amine solution with a certain concentration of acid gases. The gas phase is repeatedly analyzed after a certain time interval, until two or three similar readings indicate that equilibrium has been reached. This method is called the 'Dynamic Method'.

Mason and Dodge[25] used this method to measure CO_2 partial pressures ranging from 0.19 to 14.9 psia. Leibush and Shneerson[23] used it for H_2S partial pressure measurements when the partial pressures were less than 6.7 psia; also for measuring solubilities of mixtures of CO_2 and H_2S when partial pressures of CO_2 plus H_2S were less than 3 psia. This method was also used by Atwood et al.[1] when partial pressure of H_2S was between 0.0005 to 5720 mm of mercury. Lyudkovskaya and Leibush[24] used it for CO_2 partial pressure measurements in the range of 36.8 psia to 588 psia: Riegger, Tartar and Lingafelter[29] employed this method for measurement of H_2S partial pressure in the range of 25 to 700 mm of mercury. Muhlbauer and Monaghan[26] also used dynamic method for acid gas solubility studies at 25°C.

c) Circulation Method:

In this method the vapor phase is circulated through the equilibrium cell in a closed loop. A magnetic pump or some other pumping device is used to circulate this vapor phase. TO analyze the vapor phase a small part of the circulating vapor is bled to a sampling cell.

Lee, Otto and Mather[17,18,19,20,21,22] used this method to obtain solubility data for H_2S or CO_2 or their mixtures in MEA or DEA over a wide range of conditions. Muhlbauer and Monaghan[26] also used this method for pressures ranging from 1 to 1000 mm of mercury.

Murzin et al.[27] combined dynamic and circulation methods and termed it 'Flow-Circulating' method. This method is often used in kinetic studies[31]. In this method gas circulates in a closed system and equilibrium between phases sets in during multiple bubbling of gas through the fluid layer. In the meantime, the gas flow is continuously forced in a closed cycle and equal flow equilibrium gas phase is withdrawn. The gas flow forced in as well as that withdrawn is only a small part (up to 5%) of the overall flow, therefore supply of pure gas into the system does not substantially alter the equilibrium and at the same time sampling of sufficient quantity of gas is made possible.

B. Selection of a Method for This Work:

The static method is not suitable for measurement of low partial pressures because the large sampling of gas phase for analysis can substantially disturb equilibrium in the system. Besides at very low partial pressures of acid gases a very long time is needed before equilibrium is established[27]. Since the apparatus in this work had to be used for very low partial pressure measurement (of acid gases) it was obvious at the outset that this method was not reliable.

The circulation method was also rejected because for measurement of small partial pressures it requires the circulation of a large quantity of gas and this makes the method excessively cumbersome[26,27].

The dynamic method has the advantage that a sufficient quantity of the vapor phase is continuously available for analysis. Thus gas phase analysis in no way affects the equilibrium. Also, if the flow rate of the carrier gas (e.g. N_2 in this case) is chosen carefully equilibrium is reached within a reasonable time interval. This method has the disadvantage that at higher temperatures, the amine concentration changes due to evaporation of water unless a high gauge pressure is maintained. But the amine concentration changes can be controlled to within reasonable limits by a slightly higher absolute pressure than the partial pressure of water plus amine at that temperature and by maintaining a low flow rate of N_2 through the saturators.

Two alternate routes are available in the dynamic method itself:

a) Solution Saturation Method:

Here a carrier gas of known composition viz. N_2 containing acid gas(es) is passed through a series of saturators. Equilibrium is indicated when inlet and outlet gas compositions are identical.

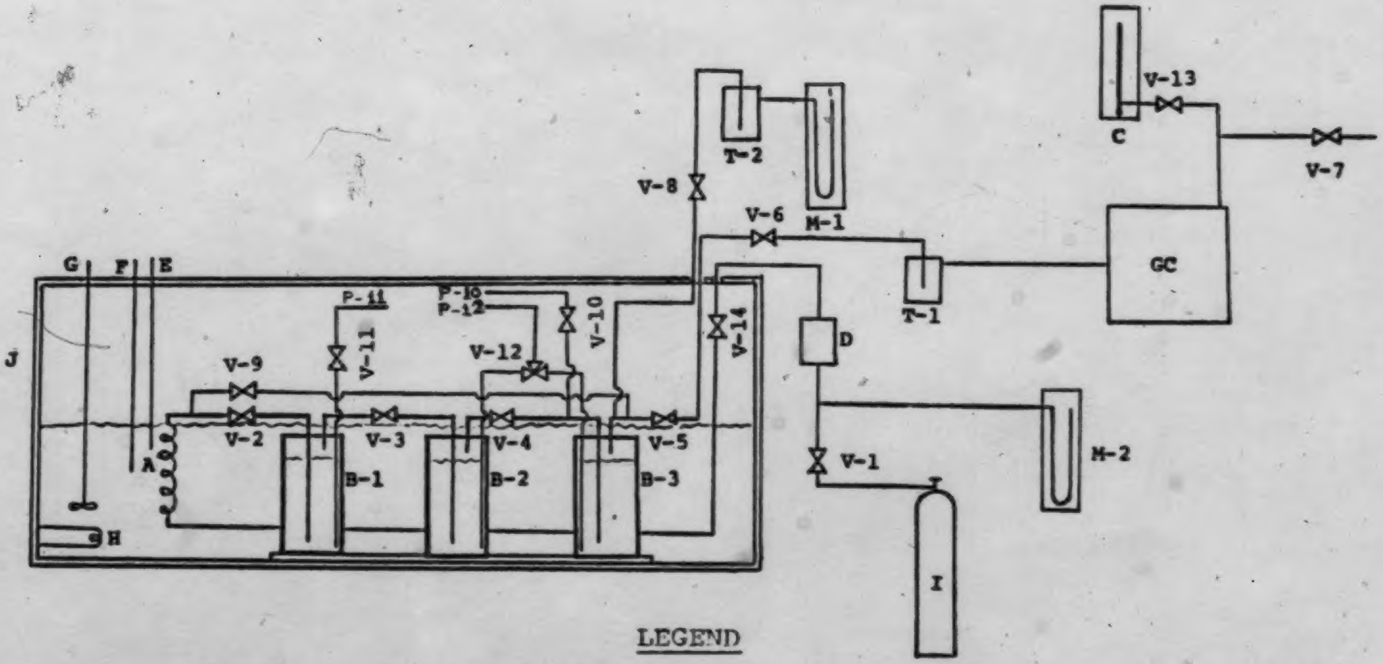
b) Gas Saturation Method:

Pure carrier gas (N_2) is passed through a number of saturators containing amine solution with acid gas(es).

Since this work had to be carried out in the region where partial pressures of CO_2 and H_2S were always less than 1 psia the gas saturation method was chosen. The obvious reason being that it is not practical to have a uniform concentration of acid gas(es) in the carrier gas when the partial pressure of these acid gases is extremely low[1] (e.g. below 0.1 psia).

C. Description of the Apparatus:

The apparatus used for this work was quite simple and is shown schematically in Figure 1. Basically it consisted of three identical 250 ml gas washing bottles connected in series. These bottles were kept in an oil bath. Carrier gas (N_2) passed through a 25 foot long, 0.25 in. O.D. stainless steel coil immersed in the oil along with most connections and all the three bottles. After passing through the heating coil N_2 was bubbled through the three saturators in series. N_2 flow was regulated by a needle valve to make sure that the flow rate was constant. The three saturators contained aqueous amine solution with a certain concentration of acid gas(es). This solution was prepared by passing the acid gas(es) through the amine solution in a separate bottle. After the saturators N_2 saturated with water and acid gas(es) passed through a trap to remove water droplets before going to the gas chromatograph (GC), and finally to the exhaust line. The gas continuously passed through the GC sampling loops; therefore gas phase monitoring was possible at whatever time intervals desired, without disturbing the system. The pressure in the final saturator was indicated by a mercury or water manometer depending on whether high or low gauge pressure was being maintained. Liquid samples were withdrawn from the last bottle by a *back-forcing method* to be described later.



LEGEND

A: Preheating Coil
B-1, B-2, B-3: Saturators
C: Soap-bubble Flow Meter
D: Rotameter
E: Thermometer
F: Thermotrol Sensor
G: Stirrer
H: Heating Element
I: N_2 Cylinder
J: Oil Bath
M-1, M-2: Manometers
T-1, T-2: Traps for Water Droplets
V-1 to V-13: Flow Regulating Valves
V-14: Check Valve

Figure 1 - Schematic Diagram of the Apparatus

All interconnecting lines were of seamless stainless steel tubing except at inlet and outlet of the gas washing bottles which had glass ball and socket joints. Glass and metal were connected by Kovar-to-borosilicate glass seals. Only stainless steel valves and connections were used because of the corrosive nature of the acid gases (especially H_2S) and the amine solutions.

Glass tubing fused from the side of the bottle and reaching the bottom of the bottle (from inside) was used for filling and discharging of the amine solutions. These lines, too, were connected by Kovar-to-borosilicate glass seals to stainless steel tubing through a ball and socket joint. The operation of filling, discharging and cleaning of the bottles without removing the apparatus from the oil-bath will be described later in the section on experimental procedure.

The traps used before the GC and the manometer to remove condensed water drops were simply 250 ml erlenmeyer flasks with a side arm which served as an outlet line. The inlet stainless steel tubing passed through an air tight rubber stopper. The outlet lines from the traps were of polyethylene plastic because the vapor phase had cooled to near room temperature. The trap near the manometer was used to prevent any vapor from reaching the column of mercury if a leak developed in the line connecting the last bottle to the manometer.

For indication and approximate measurement of gas flow rate through the system, a rotameter was used before the carrier gas entered the saturators. A similar rotameter was initially used before the gas entered the GC, but this had to be replaced by a *soap-bubble* flow meter, because of the moist nature of the gas which caused the indicator to stick in place at low flow rates. A flow meter is desirable after the GC because in the event of a leak in the apparatus the two flow meters (one before the saturators and the other after them) would give different flow rates. The *soap-bubble* flow meter (after the GC) was found to be adequate. The only disadvantage in using a *soap-bubble* flow meter was that it sometimes affected the pressure in the system since the line to the exhaust had to be closed to divert flow through the *bubble-meter*.

The saturators were mounted on a stainless steel platform with a heating coil surrounding them on supports from the platform. This assembly was immersed in oil but all the valves were above the oil surface and could be reached easily. Filling-discharging lines and the liquid sampling lines could also be reached conveniently.

The bath consisted of a 3 foot x 2 foot x 1.5 foot rectangular stainless steel container containing about 40 gallons of Grade-30 motor (mineral) oil as the heating medium. The outer walls were covered by styrofoam insulation and the bath was enclosed in a hardboard casing. Agitation of oil was obtained by a stirrer rotated by a 0.25 HP electric motor mounted on the cover of the bath. Heating was accomplished by a 1500 watt, 220 volt cylindrical heating element (General Electric) which was screwed into the bath about 4 inches above the bath floor. The heater was connected to a Hallikainen Instrument Thermotrol, which controlled the bath temperature to within ±0.01°C. The sensor from the temperature controller was passed into the oil through a hole in the bath cover. The temperature of the bath was indicated by two pre-calibrated thermometers,one in the middle and the other at the end of the cover.

The gas inlet, gas outlet and the line to the mercury (or water) manometer came out of the bath through two holes in the bath cover. These lines had stainless steel *quick-connects* so that the apparatus inside the bath could be disconnected conveniently whenever needed. A small lid just above the *saturator-assembly* allowed access to the valves and for liquid sampling, filling, discharging and cleaning of saturators. At other times the lid was kept closed to minimize the escape of oil vapors.

D. Operating Details:

a) Start-Up:

The bottles were filled with desired amine solution and lowered on the stainless steel platform which held them in place. The ball and socket joints were properly greased (with Dow Corning high vacuum silicone grease) and clamped. The whole assembly was lowered into the oil bath with only the inlet, outlet and manometer lines coming out of the top of the bath through two holes. These lines were connected to the manometer, inlet gas line and outlet line to the GC, through quick-connects. At this time all the valves were in the closed position. The stirrer was turned on and after some turbulence in the oil had been obtained, the heater along with the thermotrol (temperature controller) were turned on. The thermotrol reading was set through a calibration curve obtained earlier. It took a few hours for the bath to reach a desired temperature. For example, it took about 6 to 7 hours for the bath to reach 100°C from room temperature.

b) Establishment of equilibrium:

Once the temperature of the bath had reached a steady value, carrier gas (N_2) flow through the saturators was started. A nitrogen pressure of about 5 psig was first set. Then valves 1, 2, 3, 4, 5, 6 and 7 were opened in that order. A small change in mercury level in the manometer, M-2, showed that gas had started flowing through the system. Also the rotameter showed flow of N_2 through the system. Now valve-13 was opened and then valve-7 closed, to measure the flow rate of carrier gas through the saturators by the *soap-bubble* meter. If the flow rate was above 15 ml/min valve-1 was closed slightly until the rate reached about this value. The final flow rate setting was obtained by the fine-metering valve-6. A N_2 flow rate of about 10 ml/min was found to be the optimum. Once the desired flow rate had been obtained valve-7 was opened again and valve-13 closed. Valve-8 was now opened to connect the last saturator, B-3, to the manometer, M-1, which gave the gauge pressure in B-3.

For temperatures up to 80° C, N_2 flow through the amine solution did not affect the amine concentration much because the partial pressure of 2.5 normal aqueous MEA solution is about 2.8 psia[7] at 60°C and 6.6 psia[7] at 80°C. About 4 hours were allowed for the N_2 to flow through the saturators. After that the gas composition was monitored every half-hour using the GC. The gauge pressure from M-1 was also noted each time. When two identical GC analysis had been obtained and M-1 readings were also almost the same,equilibrium had been established. To make sure one hour more was allowed and M-1 and GC readings taken again. If these readings were similar to the previous ones establishment of equilibrium was confirmed. Liquid samples were now taken using the method described later.

For a temperature of 100°C the partial pressure of 2.5 normal aqueous MEA solution was about 13.7 psia[7] which was slightly above atmospheric pressure. Therefore to avoid excessive removal of water and hence appreciable change in amine concentration an absolute pressure of about 15 to 16 psia was maintained in B-3. This was achieved by closing valve-5 slightly in combination with valve-6 to maintain a flow rate of carrier gas around 10 ml/min. In the case of 5 normal MEA solution the partial pressure of water plus MEA was about 13 psia[7]. Therefore, an absolute pressure of about 14.5 to 15 psia kept the amine normality change within desirable limits. N_2 was allowed to flow through the saturators at 10 ml/min for about 3 hours before starting the monitoring of the vapor phase. Monitoring was continued every half hour until consistent readings were obtained. A close watch was kept on M-1 to make sure that gauge pressure did not vary much between monitorings because a change in pressure disturbs the equilibrium. Micrometering valve-6 was used to maintain this pressure to a near constant value. Once two consistent readings of GC and M-1 were obtained, equilibrium had been reached and liquid sample was now taken. The time needed to reach equilibrium depends on the acid gas concentration in the liquid phase. For higher concentrations it usually took about 4 to 5 hours if the gauge pressure in B-3 was maintained around a certain value. For lower acid gas concentrations a little longer time was usually needed.

c) Liquid sampling:

Once the GC analysis of the vapor phase had shown that equilibrium had been reached and also a reading of the manometer, M-1, had been taken, it was time for obtaining a representative sample of the liquid phase. Saturator B-3 was the one with which the gas phase was in contact last and hence the liquid sample was withdrawn from B-3. To do this valves 2, 4, 5 and 8 were closed. Valve-9 was now opened to apply a slight back pressure on the liquid in B-3. Valve-10 was now opened. Liquid was forced through the fritted glass end in B-3 through valve-10 and into a liquid sampling bottle at port, p-10. The first 5 to 10 ml of the sample were discarded since they had flushed the line and contained some drops from the previous sample. After this flushing about 10 ml were collected in a liquid sampling bottle which was then stoppered and allowed to cool to room temperature before chemical analysis.

d) Discharging, Cleaning and Refilling of Saturators:

To discharge amine solution the bottles were emptied in the order: B-3, B-2 and finally B-1. Valve-9 and then the three-way valve-12 for B-3 were opened. All the other valves except 1 were closed earlier. The discharged solution was collected in the *filling-bottle* or a container at port, p-12. Once B-3 had been emptied valve-4 was opened and valve-12 was turned towards B-2. Contents of B-2 were again collected at port p-12. After B-2 had been emptied valves 3 and then 11 were opened to discharge the contents of B-1 at port, p-11.

Filling of the bottles could be accomplished in any order desired. To fill B-1, a *filling-bottle* was connected to p-11. Valves 11, 3, 4, 5, 6 and 7 were then opened in this order. Amine solution (or cleaning liquid) was forced into B-1 by applying N_2 pressure above the liquid in the *filling-bottle*. Once B-1 had been filled with a desired solution, valves 11 and 3 were closed. The *filling-bottle* was now connected to p-12 and valve-12 was opened for B-2. N_2 pressure on liquid, in the *filling-bottle*, forced it into B-2. After B-2 had been charged valve-4 was closed and valve-12 opened for B-3. B-3 was filled in the same way as the other two bottles.

For cleaning of the bottles warm distilled water (or amine solution) was pushed into each bottle using the technique described for filling of the bottles. N_2 was bubbled through this liquid for a few minutes (for proper rinsing) and then the liquid was removed using the procedure described for discharging.

Note that when the saturator assembly was at a high temperature (above 80°C) cleaning liquid or new amine solution was warmed before charging to prevent cracking (or breaking) of the glass due to sudden contraction.

E. Analytical Methods:

a) Gas Phase Analysis:

A model 5710A Hewlett-Packard gas chromatograph equipped with a Model 1750A disc integrator recorder was used for all gas phase analyses. The column was a 10 foot long, 0.25 in. O.D. stainless steel tube filled with CHROMOSORB-104 packing. The column was kept at 130°C for H_2S and 110°C for CO_2 or for CO_2 and H_2S mixtures.

b) Liquid Phase Analysis:

In this work both direct titration methods and methods which rely on the evolution of CO_2 and/or H_2S were tested for the chemical analysis of the acid gases. It was found that for very small concentrations (less than 0.1 mole acid gas(es) per mole of amine) of CO_2 and H_2S the evolution methods are not reliable since the quantity of sample available for analysis was small (about 10 ml). Also almost always a fraction of the acid gas(es) remained in the liquid no matter how much the technique was refined. A brief description of the analysis methods tried follows:-

Method-1:

Dow Method; Iodometric Determination of evolved H_2S: H_2S was evolved from an aliquot portion of the liquid sample by addition of concentrated sulphuric acid and boiling. Purified air was drawn in by aspiration through the evolution flask carrying the evolved H_2S through a reflux condenser, then through a gas scrubber containing a known volume of standard iodine solution. Excess iodine was determined by titration with standard sodium thiosulphate solution.

Method-2:

H_2S by Iodine-Thiosulphate Titration:- The method is that outlined by Kolthoff and Sandell[14]. An aliquot portion of the liquid sample was put into acidified iodine solution. Excess iodine was back titrated using standard sodium thiosulphate solution. Sulphuric acid in iodine should be at least 18 moles per mole of DEA or 11 moles per mole of MEA.

Method-3:

H_2S by Arsenite-Iodine Titration[2]:- Here Arsenious sulphide was precipitated by H_2S and the excess arsenite was back titrated using iodine solution. The reaction for this precipitation is:

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

The problem with this method was that a large volume (about 20 ml) of sample was needed for reliable results. With about 2 to 3 ml liquid samples reproducible results were not obtained.

Method-4:

H_2S by direct I_2 titration: An aliquot of sample was titrated directly with 0.1 normal standard iodine solution in a medium buffered with sodium bicarbonate.

Method-5:

Dow method for CO_2[6]: CO_2 was evolved from an aliquot portion of the sample by addition of concentrated sulphuric acid and heating. Evolved CO_2 was carried through a reflux condenser by purified air drawn in through an aspirator and then absorbed in a known volume of 0.1 N Barium Hydroxide ($Ba(OH)_2$). The excess $Ba(OH)_2$ was determined by titration with 0.1 normal hydrochloric acid to the phenolphthalein end point. Again the problem with this method was that to use up a reasonable amount of $Ba(OH)_2$ a large amount of liquid sample was needed, especially for very low concentrations of CO_2. Since a large liquid sample was not feasible, this method was discarded.

Method-6:

CO_2 by precipitation as $BaCO_3$: The CO_2 in an aliquot portion of the sample was precipitated as Barium Carbonate ($BaCO_3$) in the presence of excess Barium Chloride ($BaCl_2$). The solution was filtered and the $BaCO_3$ precipitate was titrated with 0.1 normal hydrochloric acid using modified methyl orange (Methyl Orange - Xylene Cyanol solution) indicator.

Determination of Amine Concentration: The amine concentration in the liquid was determined by titration of an aliquot of the sample with about 0.1 normal sulphuric acid solution employing methyl red as an indicator.

F. Selection of Methods for Liquid Analysis:

As mentioned earlier methods relying on evolution of acid gas(es) were not reliable at very low concentrations of acid gases in the amine solution. Therefore, these methods were not pursued after preliminary tests. Out of the direct titration methods for H_2S, Method-4 always gave a larger value of H_2S composition in the amine solution as compared to iodine-sodium-thiosulphate method

(Method-2). Data in the literature were reproduced within reasonable limits using the iodine-thiosulphate method, while with Method-4 the H_2S partial pressure was always lower for the determined H_2S composition using this method. This indicated that liquid phase H_2S determination was incorrect in the positive direction i.e., Method-4 always gave a higher H_2S composition than actual. Later it was found that this was due to the fact that some iodine was used up by thiosulphate ($S_2O_3^{2-}$) present in a sample. If the amount of iodine used up by thiosulphate was determined and then subtracted from the total, the iodine consumed by H_2S was obtained. This gave results which were nearly identical to those given by iodine-thiosulphate (Method-2) method. Since reliability of iodine-thiosulphate titration has been confirmed before[14] and since determination of thiosulphate in a sample is quite cumbersome, the iodine-thiosulphate method (Method-2) was adopted and used for all the H_2S analysis.

As for CO_2 Method-6 was found to be good. It reproduced data in the literature reasonably well and also gave reproducible results. Its only disadvantage is that it is slightly cumbersome. Because of absence of any other reliable and less cumbersome technique for CO_2 analysis in the literature, this method was used for all CO_2 determinations.

The method used for amine analysis is the one used by Girdler Corporation, Louisville, Kentucky (SM-1M for MEA; SM-1D for DEA). This method was tested by preparing a standard amine solution and was found to be very accurate and reliable.

G. Details of the Methods Used for CO_2, H_2S And Amine Determinations:

a) CO_2 Determination (Method-6)

Procedure: About 20 to 25 ml of distilled water was heated in a 250 ml erlenmeyer flask. Once the water had started boiling approximately 2 grams of solid $BaCl_2$ were added. The flask was swirled to dissolve the $BaCl_2$. Immediately by a syringe 2 ml of the sample solution was added to the flask. The flask was removed from heat and allowed to stand for about five minutes for the white precipitate to settle down somewhat. The flask was then stoppered and cooled under cold tap water for about ten minutes. Three 7 cm 41 Whatman ashless filter papers were placed in series in a 7 cm Büchner funnel placed in a large erlenmeyer flask with the sidearm attached to a water aspirator. Slowly the precipitate was poured on to the filter papers. The flask containing the precipitate was washed with two 25 ml portions of distilled water. Each washing was transferred to the filter paper. The filtrate was discarded. The filter papers with the washed precipitate were transferred to the erlenmeyer flask which had the precipitate previously and about fifty ml of distilled water were added to it. The contents of the flask were swirled with a magnetic stirrer, until the filter paper had been torn into small pieces (this puts almost all the precipitate in solution and therefore, it is easier to titrate). Approximately five drops of modified methyl orange indicator (Methyl Orange - Xylene Cyanol solution) were added to the flask and the mixture titrated with about 0.1 normal hydrochloric acid. The mixture was titrated to a grey end point. Any barium carbonate precipitate sticking to the sides of the flask was washed down with distilled water and the titration continued to the same grey end point.

b) H_2S Determination (Method-2)

Procedure: 20 ml of 0.1 normal standard iodine solution was pipetted into a 500 ml erlenmeyer flask. The proper excess of sulphuric acid for the size of amine sample aliquot was added. (The ratio of sulphuric acid to DEA should be at least 18 moles H_2SO_4 per mole of DEA and 11 moles sulphuric acid per mole of MEA). The magnetic stirring bar was now put in and by a syringe 2 ml aliquot of sample was added while stirring. The excess iodine was back titrated with standard 0.1 normal sodium thiosulphate solution to a light yellow colour. About 5 ml of 0.2

percent starch indicator solution was now added and the titration continued to the change from blue-black to *water-white* colour.

c) MEA (or DEA) Determination:

Procedure: To an erlenmeyer flask containing about 100 ml of distilled water, two ml of sample solution were added. A few drops of methyl red indicator were added until the colour was distinctly yellow. The solution was then titrated using ca. 1 normal sulphuric acid. The end point was indicated by change in colour of solution from yellow to pink.

CHAPTER II

EXPERIMENTAL RESULTS AND THEIR COMPARISON

This chapter presents in graphical form, the expermental data obtained in this work.

To test the apparatus, initial measurements were made for conditions of solution strength and temperatures for which some data were available in the literature. Measurements were made for pure H_2S and pure CO_2 in 2.5 N MEA at 80° and 100°C. For the two 100°C isotherms and the 80°C isotherm for H_2S, some data points, for low loadings of acid gases (ca 0.1 moles/mole of MEA and less), have been obtained by Jones et al.[9], and Garst and Lawson[33]. These points have been plotted on the same figures. In this work, data were also obtained for mixtures of CO_2 and H_2S in 5 N MEA at 100°C. The loadings of H_2S and CO_2 were less than ca. 0.12 moles/mole of MEA. For these low acid gas concentrations, no data have been published to date.

Figures 2 and 3 present the 80°C isotherms for pure H_2S and CO_2 in 2.5 N MEA. Figures 4 and 5 show the 100°C isotherms for pure H_2S and CO_2 in 2.5 N MEA. Smoothed mixture data, for CO_2 and H_2S in 5 N MEA at 100°C, are plotted in Figures 6 and 7. The raw experimental data are tabulated in Appendix B.

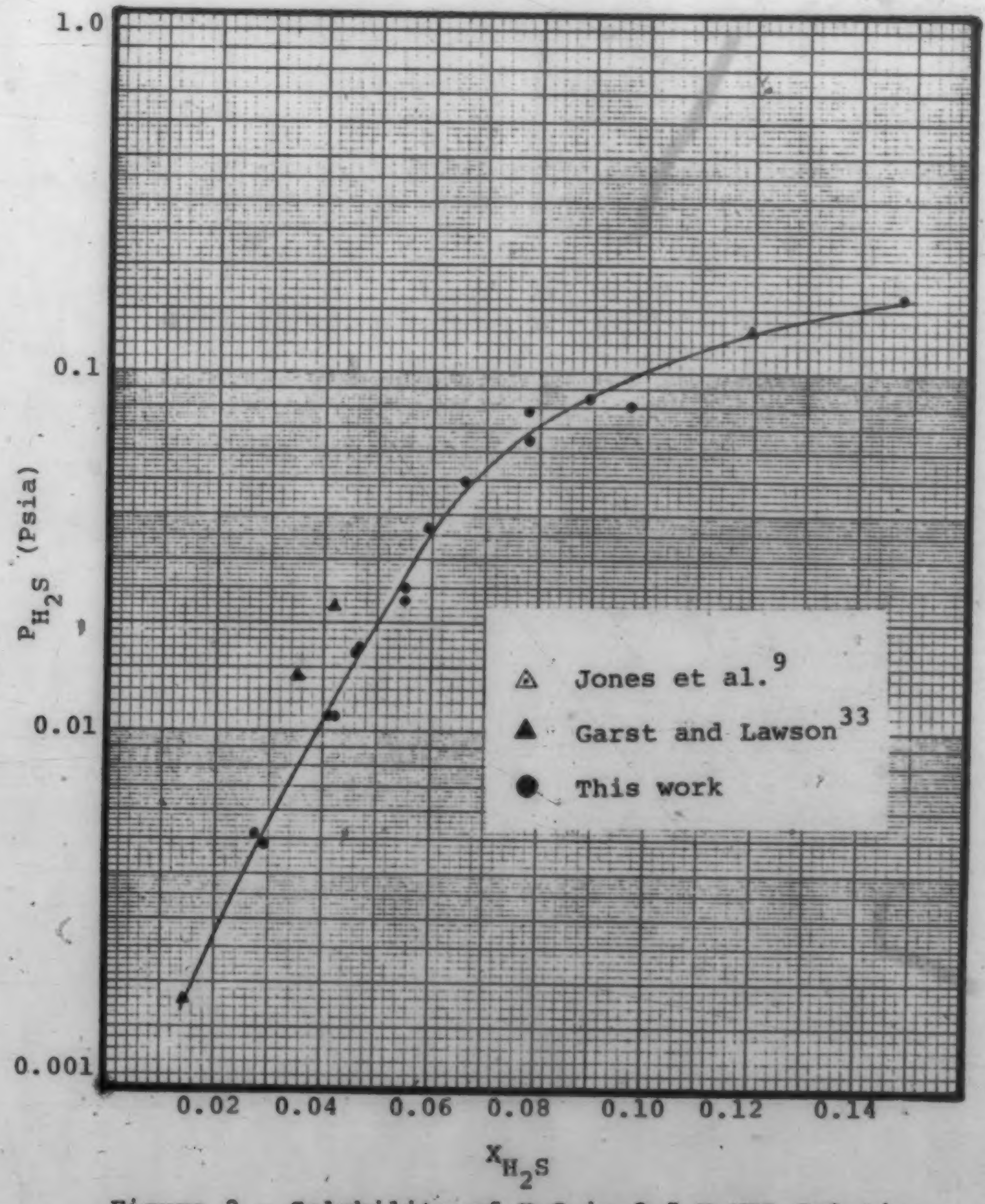


Figure 2 - Solubility of H_2S in 2.5 N MEA Solution at 80°C.

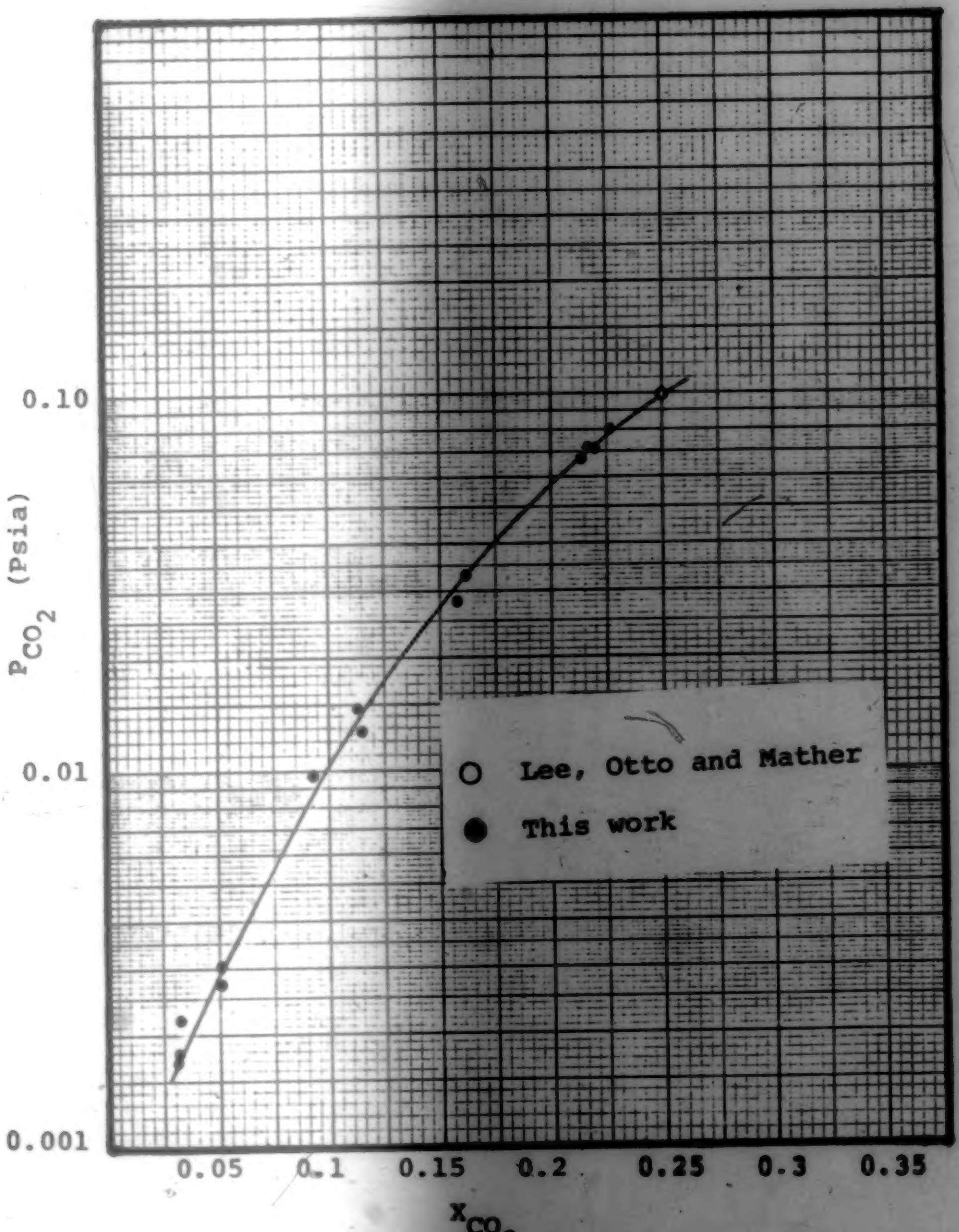


Figure 3 - Solubility of CO_2 in 2.5 N MEA Solution at 80°C.

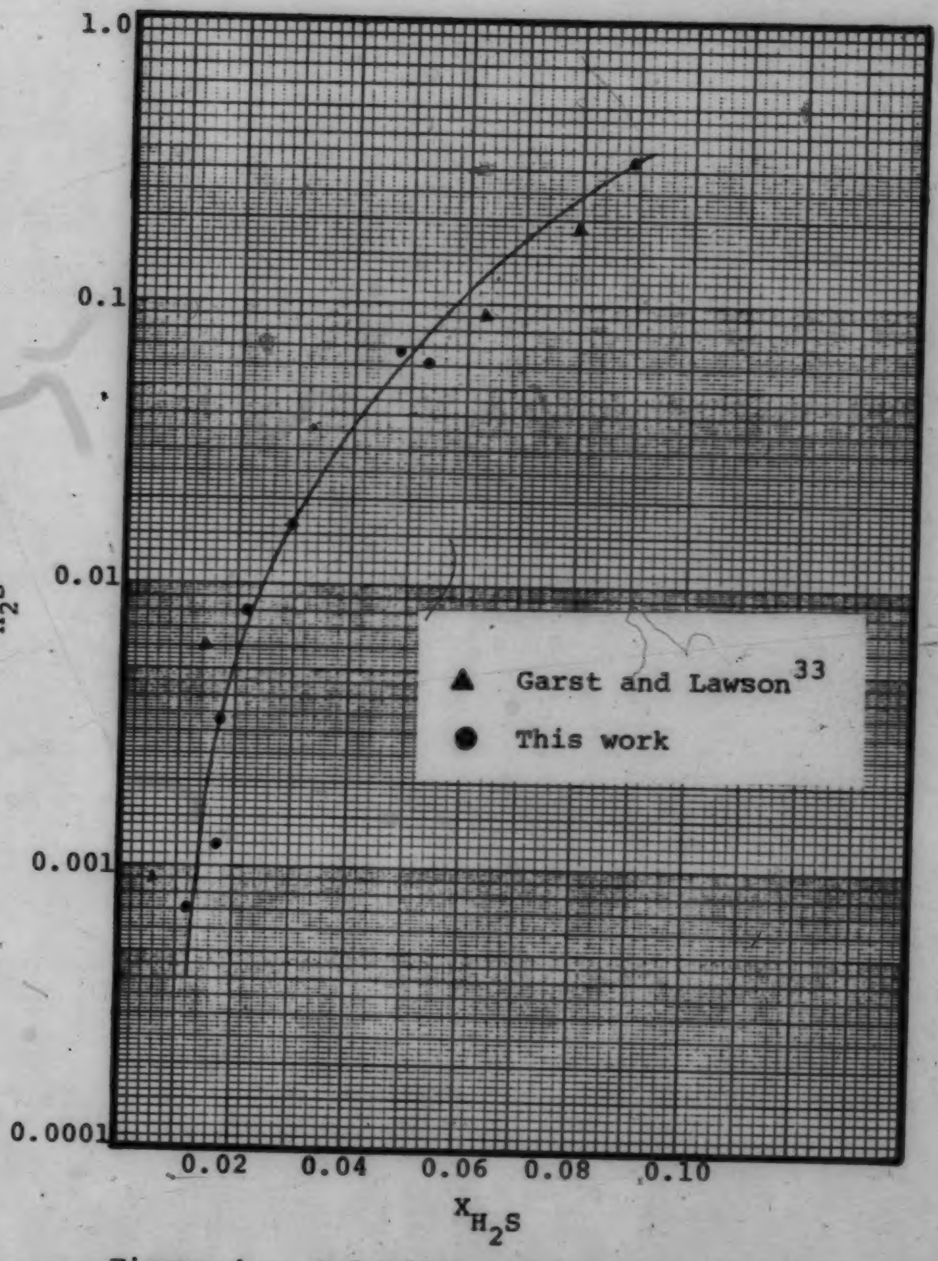


Figure 4 - Solubility of H_2S in 2.5 N MEA Solution at 100°C.

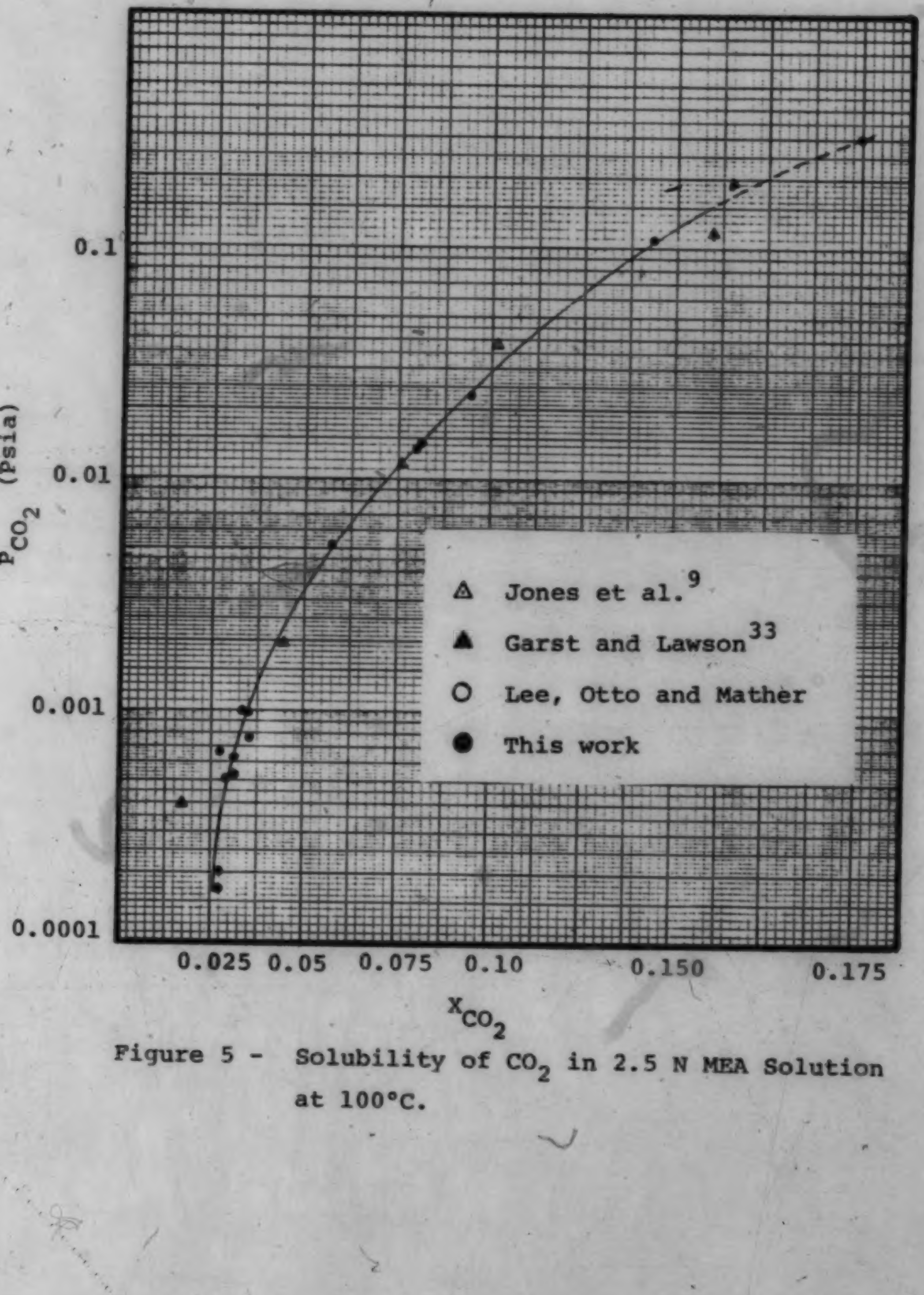


Figure 5 - Solubility of CO_2 in 2.5 N MEA Solution at 100°C.

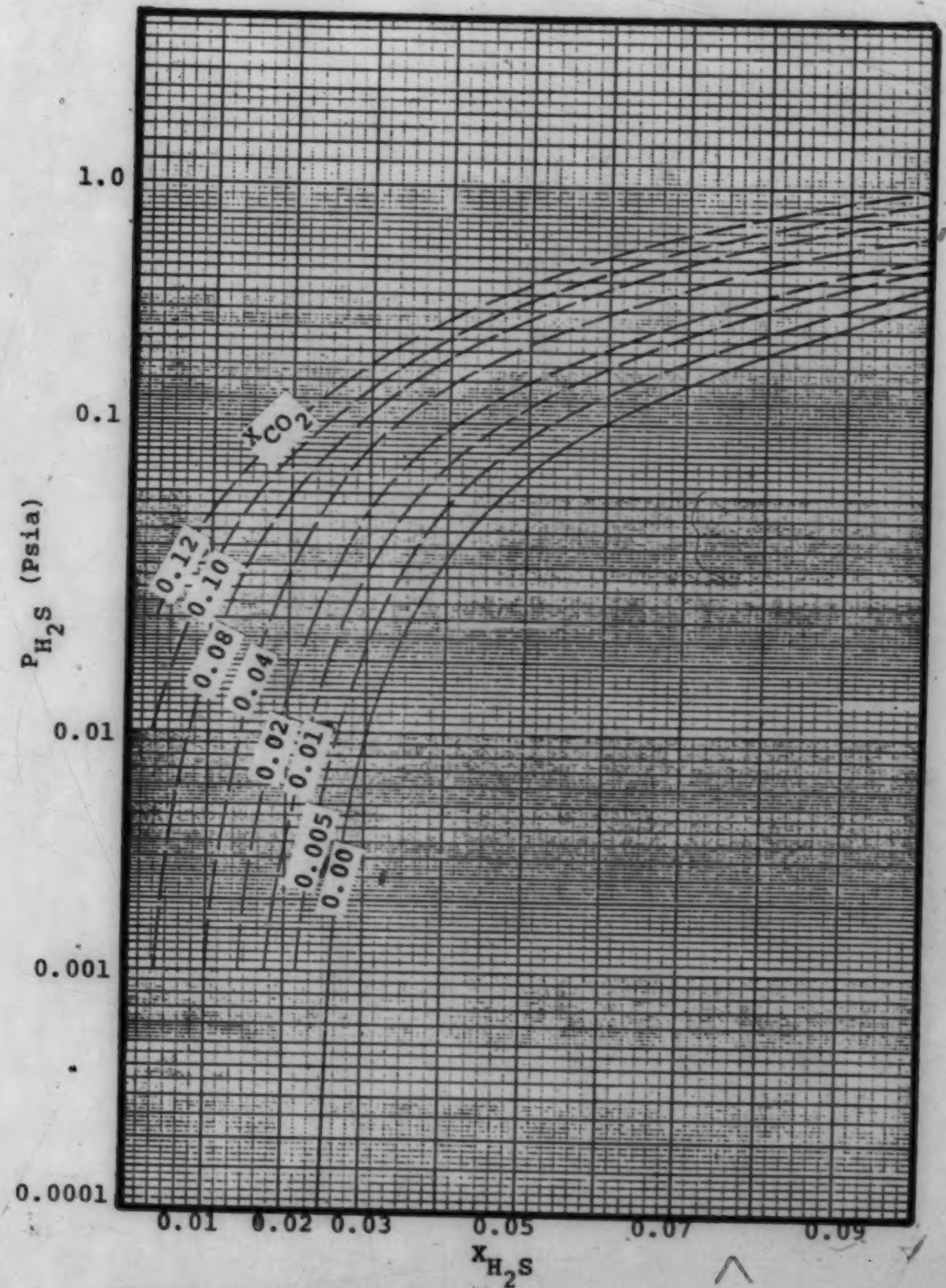


Figure 6 - Effect of CO_2 on the Partial Pressure of H_2S Over 5 N MEA Solution at 100°C.

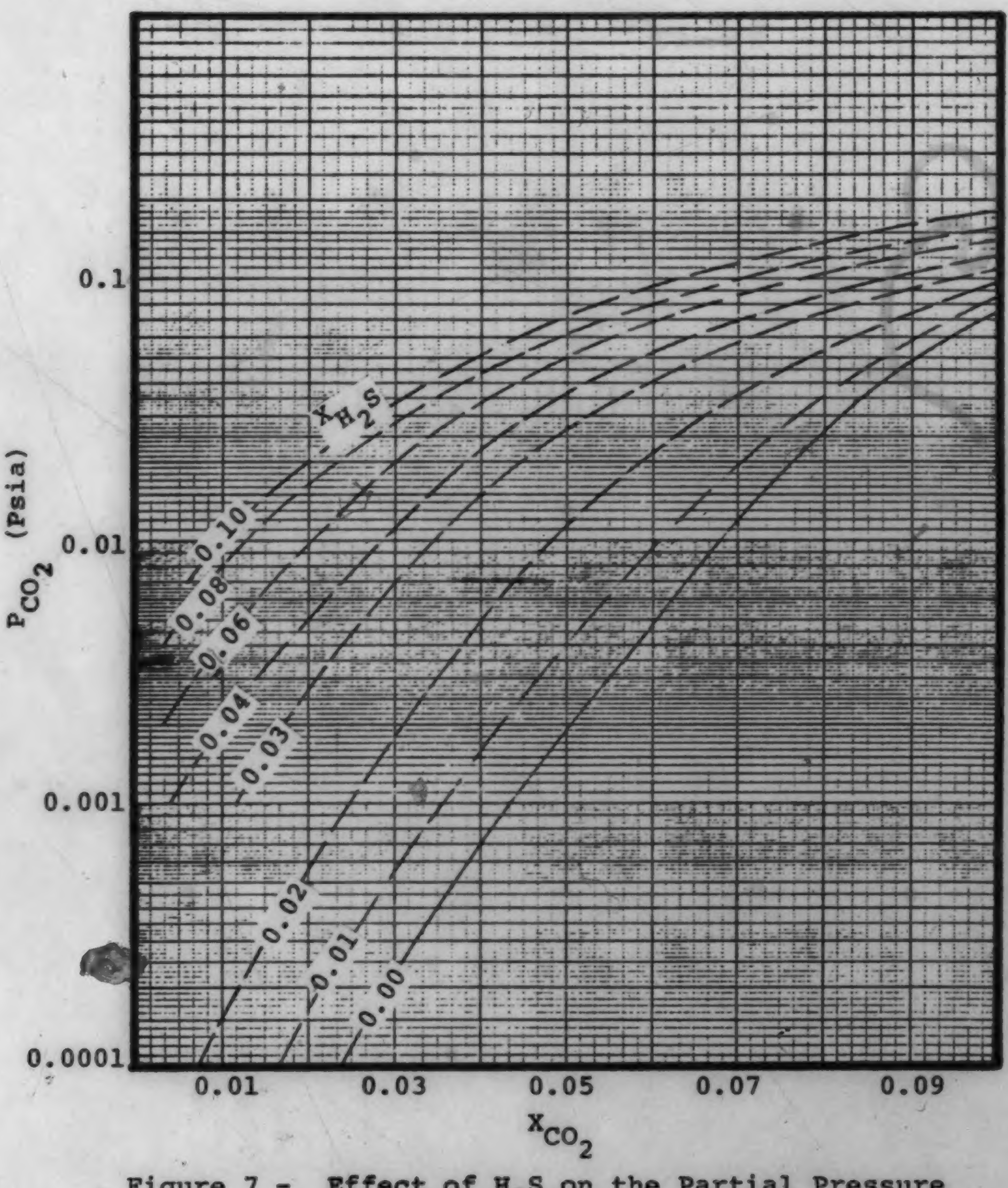


Figure 7 - Effect of H_2S on the Partial Pressure of CO_2 Over 5 N MEA Solution at 100°C.

CHAPTER III

THEORETICAL PREDICTION OF PARTIAL PRESSURES OF H_2S and CO_2

While the solubility data are useful in themselves, it is desirable to have a computer-oriented correlation which reproduces the experimental results. It would also be useful for regions where no data are presently available.

A number of researchers have attempted to correlate the solubility data for CO_2 and/or H_2S in ethanolamine solutions. A common starting point for all the thermodynamic models proposed so far is the postulation of reactions occuring in the solution. For simple systems, i.e. systems containing either H_2S or CO_2 in aqueous ethanolamine (EA) solution, correlations have been proposed by different authors. Atwood et al.[1] proposed a correlation for predicting partial pressures of H_2S in aqueous ethanolamine solutions based on chemical reactions taking place in the solution. Klyamer[11] made slight modifications in the above correlation and has also made some comparisons with experimental data. Klyamer and Kolesnikova[12] discussed a general mathematical description of experimental data for the thermodynamic equilibrium in the CO_2-water-MEA(DEA) systems. In postulating the equilibrium equations they have accepted the assumptions made by Atwood et al.[1]. They found that the maximum error in the calculated values compared to the experimental ones for a given set of conditions was not larger than 20 percent of CO_2 partial pressure. Theoretical treatment of equilibria for the absorption of CO_2 into aqueous ethanolamine solutions has also been discussed by Danckwerts and McNeil[4].

More recently Klyamer et al.[13] have proposed a thermodynamic model for predicting equilibrium partial pressures of acid gases in aqueous ethanolamine solutions. They have obtained equations which describe the functional dependence between the partial pressure of the acid gas components and the composition of the solution at various temperatures. In essence, their model combines the chemical equations postulated for the simple systems, H_2S-water-EA and CO_2-water-EA, and also incorporates the assumptions made for these simple systems by other authors.

Most recently (while this work was in progress) Kent and Eisenberg[10] presented a modified version of the Klyamer et al.[13] model. This model is essentially based on postulation of similar reactions as those of the Klyamer et al.[13] model; however, all the non-idealities have been incorporated into only two parameters.

Both the Klyamer et al.[13] and the Kent and Eisenberg[10] Models are discussed in detail in the following pages along with the modification in Klyamer et al. model.

A. Correlation Based on the Thermodynamic Model of Klyamer et al.[13]:

The assumptions made in postulating the chemical reactions are listed below:

a) The salts (bisulphides, carbonates and carbamates) which are created by the absorption of H_2S and CO_2 are fully dissociated[1,11,12].

b) The activity coefficients of different ions in solution are equal and independent of temperature[1].

c) The activity of water is equal to its molarity[1].

d) The physical solubility of CO_2 or H_2S is not changed by the addition of ethanolamine (EA) and salts of EA[1,12].

On the basis of the above assumptions the following reactions for the H_2S-CO_2-water-MEA systems can be written:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \qquad \text{----------(a)}$$

$$H_2S \rightleftharpoons H^+ + HS^- \qquad \text{----------(b)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{----------(c)}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad \text{----------(d)}$$

$$2RNH_2 + CO_2 \rightleftharpoons RNH_3^+ + RNHCO\bar{O} \qquad \text{----------(e)}$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad \text{----------(f)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad \text{----------(g)}$$

where R stands for $-CH_2-CH_2-OH$ group. Analogous equations may be written (to represent the reactions) for the H_2S-CO_2-water-DEA system.

The following balance equations for the reacting compounds can be formed:

Charge balance (or Electroneutrality) equation:

$$[RNH_3^+]+[H^+] = [HCO_3^-]+[RNHCO\bar{O}]+2[CO_3^{2-}]+[OH^-]+[HS^-]+2[S^{2-}] \qquad \text{----------(1)}$$

Mass balance equations:

$$[RNH_2] + [RNHCO\bar{O}] + [RNH_3^+] = m \qquad \text{----------(2)}$$

$$[HS^-] + [H_2S] + [S^{2-}] = mX_{H_2S} \qquad \text{----------(3)}$$

$$[HCO_3^-] + [CO_2] + [CO_3^{2-}] + [RNHCO\bar{O}] = mX_{CO_2} \qquad \text{---------(4)}$$

where,

m = moles of EA/1000 gm of water

X_{CO_2} = moles of CO_2/mole of EA

X_{H_2S} = moles of H_2S/mole of EA

$[C_i]$ = moles of compound (or ion) C_i/1000 gm of water (Molality).

The following thermodynamic equilibrium constant expressions can also be written:

$$K_i = \frac{\gamma^2}{a\alpha^2} \frac{[\mathrm{RNH_3^+}]\,[\mathrm{OH^-}]}{[\mathrm{RNH_2}]} \quad \text{----------(5)}$$

$$K_w = \frac{\gamma^2\,[\mathrm{H^+}]\,[\mathrm{OH^-}]}{\alpha} \quad \text{----------(6)}$$

$$K_{1C} = \frac{\gamma^2\,[\mathrm{H^+}]\,[\mathrm{HS^-}]}{[\mathrm{H_2S}]} \quad \text{----------(7)}$$

$$K_{2C} = \frac{\gamma\,[\mathrm{H^+}]\,[\mathrm{S^{2-}}]}{[\mathrm{HS^-}]} \quad \text{----------(8)}$$

$$H_{H_2S} = \frac{[\mathrm{H_2S}]}{P_{H_2S}} \quad \text{----------(9)}$$

$$K_m = \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{[\mathrm{RNH_3^+}]\,[\mathrm{RNHCOO^-}]}{[\mathrm{RNH_2}]^2\,P_{CO_2}} \quad \text{---------(10)}$$

$$K_{1Y} = \frac{\gamma^2\,[\mathrm{H^+}]\,[\mathrm{HCO_3^-}]}{\alpha\,[\mathrm{CO_2}]} \quad \text{---------(11)}$$

$$K_{2Y} = \frac{\gamma\,[\mathrm{H^+}]\,[\mathrm{CO_3{}^{2-}}]}{[\mathrm{HCO_3^-}]} \quad \text{---------(12)}$$

$$H_{CO_2} = \frac{[\mathrm{CO_2}]}{P_{CO_2}} \quad \text{---------(13)}$$

WHERE

$[RNHCOO^-]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[CO_2]$, $[H_2S]$, $[RNH_3^+]$, $[RNH_2]$, $[OH^-]$, $[H^+]$, $[HS^-]$ and $[S^{2-}]$ are respectively, the concentrations (molalities) of the carbamate, bicarbonate, carbonate ions, the physically dissolved CO_2 and H_2S, concentrations of ionized and un-ionized ethanolamine, hydroxyl ions, hydrogen ions, bisulphide and sulphide ions. P_{CO_2} and P_{H_2S} are the partial pressures of CO_2 and H_2S respectively in mm of mercury; K_m, K_{1Y}, K_{2Y}, K_i, K_w, H_{CO_2}, H_{H_2S}, K_{1C} and K_{2C} are the equilibrium constants for the formation of the carbamate, the first and second dissociation constants for H_2CO_3 (carbonic acid), EA ionization constant, water dissociation constant, the *inverted* Henry's constants for CO_2 and H_2S solubility in water, the first and second constants for H_2S dissociation. The average coefficient for the ion activity is given the symbol γ, α is the coefficient for the water activity and a is the ratio between the un-ionized ethanolamine activity and the activity of water.

Atwood et al.[1] have shown that for the system H_2S-water-EA the form of the dependence of the average value of the activity coefficients on their concentration can be taken as the same for all ions. Klyamer et al.[13] have accepted this dependence of the average value of activity coefficient of all ions on the ionic concentration for the system H_2S-CO_2-water-EA by the formulation of equations (5) to (8) and (10) to (12). Atwood et al.[1] obtained the average value of activity coefficient, γ, by assuming that the amine salts are similar to ammonium salts. They have correlated γ as a function of ionic strength of the solution. The ionic strength, μ, is defined as:

$$\mu = \Sigma \tfrac{1}{2} m_i z_i^2 .$$

m_i = molality of each ion.

z_i = electrical charge on each ion.

The values for the dependence of the correction factor, a, on the concentration of the free ethanolamine and the values of K_w, K_{1C}, K_{2C}, K_{2Y}, H_{CO_2} and H_{H_2S} in the range of temperatures 25 to 120°C were taken from the work of Atwood et al.[1]. Values of K_i, K_m and K_{1Y} as functions of temperature have been taken from earlier publications[11,12].

The analysis of equations (1) to (13) leads to the conclusion that the most important parameters which enter into many reactions are the so called degrees of sulphidation (X_{H_2S}) and carbonation (X_{CO_2}). It has been shown that the concentration of the ions S^{2-} and H^+ can be neglected for all practical cases in equations (1) to (3)[11,12]. It is necessary to take $[CO_3^{2-}]$ and $[OH^-]$ into account only at very low X_{CO_2} or X_{H_2S} (i.e. for X_{CO_2} or X_{H_2S}

approximately equal to 0.01 mole/mole of EA). If these simplifications are taken into account, the simultaneous solution of equations (1) to (13) allows derivation of expressions for the calculation of the equilibrium partial pressures of CO_2 and H_2S if the liquid phase composition and temperature are known. These expressions (as derived in Appendix C) are:

$$P_{H_2S} = \frac{K_w}{K_i\ K_{1C}\ H_{H_2S}} \cdot \frac{\gamma^2}{a\alpha} \cdot \frac{A(A+B)}{(m-z-A-B)} \tag{14}$$

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{z(A+B)}{(m-z-A-B)^2} \tag{15}$$

and

$$A = m-z-B- \frac{K_i\ K_{1\gamma}\ H_{CO_2}}{K_m\ K_w} \cdot \frac{z}{a(B-z)} \tag{16}$$

where

$$A = m\ X_{H_2S} - H_{H_2S}\ P_{H_2S}$$

$$B = m\ X_{CO_2} - H_{CO_2}\ P_{CO_2}$$

and

$$z = [RNHCO\bar{O}]$$

Equations (14) to (16) have three unknowns; P_{H_2S}, P_{CO_2} and z ($[RNHCO\bar{O}]$). Since these equations are implicit in P_{H_2S} and P_{CO_2} $[A = f(P_{H_2S})\ ;\ B = f(P_{CO_2})]$, iterative techniques have to be used for their solution.

For a degree of saturation of solutions smaller than 0.7 moles/mole of EA, the physical solubility of H_2S and CO_2 can be neglected in the balance equations[1,11,12]. It can also be assumed that for X_{H_2S} plus X_{CO_2} between 0.05 and 0.7 moles/mole of EA, CO_2 will exist as $RNHCOO^-$ and HCO_3^- ions and H_2S as HS^- ions. If these simplications are taken into account, equations (14) to (16) can be simplified to:

$$P_{H_2S} = \frac{K_w}{K_i\ K_{1C}\ H_{H_2S}} \cdot \frac{\gamma^2}{a\alpha} \cdot \frac{mX_{H_2S}\ (X_{H_2S} + X_{CO_2})}{\left\{\frac{[HCO_3^-]}{m} + 1 - X_{H_2S} - 2X_{CO_2}\right\}^2} \quad \text{---------} \ (17)$$

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{(X_{H_2S} + X_{CO_2})(X_{CO_2} - \frac{[HCO_3^-]}{m})}{\left\{\frac{[HCO_3^-]}{m} + 1 - X_{H_2S} - 2X_{CO_2}\right\}^2} \quad \text{----------} \ (18)$$

and

$$\frac{[HCO_3^-]}{m} = \sqrt{\left(\frac{\frac{K_I}{am} + 1 - X_{H_2S} - 2X_{CO_2}}{2}\right)^2 + \frac{K_I\ X_{CO_2}}{am}} - \frac{\frac{K_I}{am} + 1 - X_{H_2S} - 2X_{CO_2}}{2} \quad \text{----------} \ (19)$$

where

$$K_I = \frac{K_i\ K_{1Y}\ H_{CO_2}}{K_w\ K_m}$$

Equations (17) and (18) can be further simplified when X_{H_2S} plus X_{CO_2} are between 0.05 to 0.25 moles/mole of EA (concentrations characteristic of the regeneration process). For such cases the bicarbonate ion concentration can be neglected, and it can be assumed that CO_2 exists only as carbamate ion. Therefore, if in equations (17) and (18), $[HCO_3^-] = 0$, the following expressions are obtained:

$$P^*_{H_2S} = \frac{K_w}{K_i\ K_{1C}\ H_{H_2S}} \cdot \frac{\gamma^2}{a\alpha} \cdot \frac{mX_{H_2S}\ (X_{H_2S} + X_{CO_2}}{(1 - X_{H_2S} - 2X_{CO_2})} \quad \text{-----}(20)$$

and

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{X_{CO_2}\ (X_{H_2S} + X_{CO_2})}{(1 - X_{H_2S} - 2X_{CO_2})^2} \quad \text{--------}(21)$$

These equations are much simpler than equations (14) to (16) or (17) and (18) and, therefore, can be used for rapid estimates of partial pressures of the acid gases.

If only H_2S or CO_2 is present in the liquid phase, equations (14) to (16) can be rearranged to give an expression for P_{H_2S} or P_{CO_2}. If $X_{H_2S} = 0$, i.e. if only CO_2 is present, these equations reduce to the following form:

$$P_{CO_2} = \frac{B}{K_1} \cdot \frac{\frac{1}{2K_2} - \sqrt{(B - \frac{m}{2} - \frac{1}{2K_2})^2 + \frac{B}{K_2}} + \frac{m}{2} - B}{\frac{1}{2K_2} - \sqrt{(B - \frac{m}{2} - \frac{1}{2K_2})^2 + \frac{B}{K_2}} - \frac{m}{2} + B} \quad \text{----}(22)$$

where

$$K_1 = \frac{K_i \; K_{1Y} \; H_{CO_2}}{K_w} \cdot \frac{a\alpha^2}{\gamma^2}$$

and

$$K_2 = \frac{K_m \; K_w}{K_i \; K_{1Y} \; H_{CO_2}} \cdot a$$

When $X_{CO_2} = 0$, i.e. if only H_2S is present, the following expression for calculation of P_{H_2S} is obtained[11].

$$P_{H_2S} = \frac{m}{H_{H_2S}(1-K")} \left[\sqrt{\left(\frac{1-X_{H_2S}}{2}\right)^2 + K" \; X_{H_2S}} - \frac{1-X_{H_2S}}{2} - K" \; X_{H_2S} \right] \text{ ---- (23)}$$

where

$$K" = \frac{K_w}{K_{1C} \; K_i} \cdot \frac{\gamma^2}{a\alpha}$$

Both equations (22) and (23) are implicit and, therefore, have to be solved by iterative techniques.

Before equations (14) to (23) can be solved for any temperature and any loading of acid gas(es) all the equilibrium constants have to be known as a function of temperature. Also the correction factor, a, as a function of free ethanolamine concentration and average ionic activity coefficient (γ) as a function of ionic strength have to be known. In the literature [1,11,12,13] the equilibrium constants as functions of temperature; the correction factor, *a*, as a function of free EA concentration; and γ as a function of ionic strength have been presented in graphical form. These graphs were approximated by polynomials using the method of *least squares*, to be able to solve equations (14) to (16) by using a digital computer. The parameters for the polynomials are given in Appendix H.

The *Modified Newton Raphson Method* was used to solve the above equations. For each iteration a better estimate to P_{H_2S}, P_{CO_2} and z was obtained by the following expressions:

$$P^{i+1}_{H_2S} = P^{i}_{H_2S} - \left[\frac{f_1}{\dfrac{\partial f_1}{\partial P_{H_2S}}}\right]_{P^i_{H_2S},\, P^i_{CO_2},\, z^i} \quad \text{-------(a)}$$

$$P^{i+1}_{CO_2} = P^{i}_{CO_2} - \left[\frac{f_2}{\dfrac{\partial f_2}{\partial P_{CO_2}}}\right]_{P^{i+1}_{H_2S},\, P^i_{CO_2},\, z^i} \quad \text{-------(b)}$$

and

$$z^{i+1} = z^{i} - \left[\frac{f_3}{\left(\dfrac{\partial f_3}{\partial z}\right)}\right]_{P^{i+1}_{H_2S},\, P^{i+1}_{CO_2},\, z^i} \quad \text{-------(c)}$$

where the variables superscripted i+1 are the better estimates obtained from the previous ones, superscripted i.

Equations (14) to (16) are rearranged to give:

$$f_1 = P_{H_2S} - \frac{K_w}{K_i\ K_{1C}\ H_{H_2S}} \cdot \frac{\gamma^2}{a\alpha} \cdot \frac{A(A+B)}{(m-z-A-B)}$$

$$f_2 = P_{CO_2} - \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{z(A+B)}{(m-z-A-B)^2}$$

$$f_3 = z - \frac{a\ K_w\ K_m}{K_1\ K_{1Y}\ H_{CO_2}} \cdot (B-z) \cdot (m-z-A-B)$$

The partial differentials of f_1, f_2 and f_3 with respect to P_{H_2S}, P_{CO_2} and z, respectively, are:

$$\frac{\partial f_1}{\partial P_{H_2S}} = 1 + \frac{K_w}{K_i\ K_{1C}\ H_{H_2S}} \left[\frac{(m-z-A-B)(zA+B) + (A+B)\ H_{H_2S}}{(m-z-A-B)^2}\right]$$

$$\frac{\partial f_2}{\partial P_{CO_2}} = 1 + \frac{\gamma^2}{K_m a^2 \alpha^2} \cdot \frac{zH_{CO_2}\left[(m-z-A-B)^2 + 2(m-z-A-B)(A+B)\right]}{(m-z-A-B)^4}$$

$$\frac{\partial f_3}{\partial z} = 1 + \frac{a\ K_w\ K_m}{K_i\ K_{1Y}\ H_{CO_2}} \cdot (m - 2z - A)$$

Equations (17) to (21) were used to obtain the initial estimates of P_{H_2S} and P_{CO_2}. These initial values along with an assumed value of z were used in equations (a) to (c) to obtain better estimates. Iteration with equations (a) to (c) was continued until the difference between two successive values of each of the three variables was less than 1 percent.

B. Modifications in Klyamer et al. Model:

a) Partial pressures were substituted by fugacities in equations (9) and (13). This was considered necessary especially for low temperatures and high total pressures (pressures greater than 100 psia). The fugacity coefficient is defined as:

$$\phi_k = \frac{f_K}{P_K} \longrightarrow P_k = \frac{f_k}{\phi_k}$$

where

P_k = partial pressure of component k

f_k = fugacity of component k

ϕ_k = fugacity coefficient for component k.

The fugacity coefficients for CO_2 and H_2S were calculated using the *Modified Redlich-Kwong* equation of state. The expression for fugacity coefficient of each gas (CO_2 or H_2S) as presented by Chueh and Prausnitz[3] is:

$$\ln \phi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^{m} y_i a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_k}{RT^{3/2} b^2} \left[\ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT}$$

where

$a = \sum_{i}\sum_{j} y_i y_j a_{ij}$

$b = \sum_{i} y_i b_i$

$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj}) R^2 T_{c_{ij}}^{2.5}}{2 P_{c_{ij}}}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}}$$

$$P_{c_{ij}} = \frac{z_{c_{ij}} R T_{c_{ij}}}{V_{c_{ij}}}$$

$$V_{c_{ij}} = \tfrac{1}{2}(V_{c_i}^{1/3} + V_{c_j}^{1/3})$$

$$z_{c_{ij}} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2}\right)$$

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{\frac{1}{2}} (1 - k_{ij})$$

The molar volume, v, is that of the gas mixture, and is obtained by using the Redlich-Kwong equation of state,

$$P = \frac{RT}{v-b} - \frac{(a/T^{0.5})}{v(v+b)}$$

This equation is rearranged to give:

$$z^3 - z^2 + z(A-B-B^2) - AB = 0$$

where

$$A = \frac{aP}{R^2T^2}$$

$$B = \frac{bP}{RT}$$

and

$$v = \frac{zRT}{P}$$

The cubic equation in z (the compressibility factor) was solved and the largest real value of z was used to obtain v. After replacing P_{H_2S} and P_{CO_2} by the respective fugacities in equations (9), (10) and (13), the set of equations (1) to (13) was solved simultaneously to obtain the fugacities of H_2S and CO_2. These fugacities were divided by the fugacity coefficients of each, to obtain the respective partial pressures.

b) In all the equations used to calculate partial pressure of acid gases (equations (14), (15), (17), (18), (20), (21), (22), and (23)) the average activity coefficient, γ, appears as γ^2. This means that the accuracy in the prediction of P_{CO_2} and P_{H_2S} depends on the accuracy in the prediction of γ. As mentioned earlier γ as a function of ionic strength was obtained from the work of Atwood et al.[1]. However, when the solubility data for the system CO_2-H_2S-water-EA were used to back-calculate γ as a function of ionic strength, the simple curves reported by Atwood et al. were not obtained. Instead a family of curves was obtained depending on the initial EA concentration as well as temperature. Figure 8 shows γ as a function of ionic strength back-calculated from experimental data of Lee, Otto and Mather[15,16,17] and also of Leibush and Shneerson[23], for different temperatures and initial DEA concentrations. The thick line shows γ as a function of ionic strength obtained from the work of Atwood et al.[1]. As is evident from this figure, γ is not *only* a function of ionic strength, but is also a function of initial EA concentration and temperature. It can also be observed that γ decreases first and then increases as the concentration of ions in the solution increases (i.e. as ionic strength increases). With increasing initial EA concentration, the inflection point moves towards higher ionic strength. Theoretically this type of behavior is predicted by the *Debye-Hückel Theory*[5]. From the figure it can also be observed that the temperature dependence of γ for the same initial EA concentration is small. In conclusion it can be said, by observing Figure 8 , that the simple relationship of γ to ionic strength is inadequate. A correlation for γ which also incorporates the effects of temperature and initial EA concentration, is therefore, needed.

In this work an empirical function of temperature and initial EA concentration was added to the expression for γ vs ionic strength. The expression of γ can be written as:

$$\gamma = f_1(\mu) + f_2(T,m) \qquad (X_{H_2S} + X_{CO_2}) > 0.2 \text{ moles/mole of EA}$$

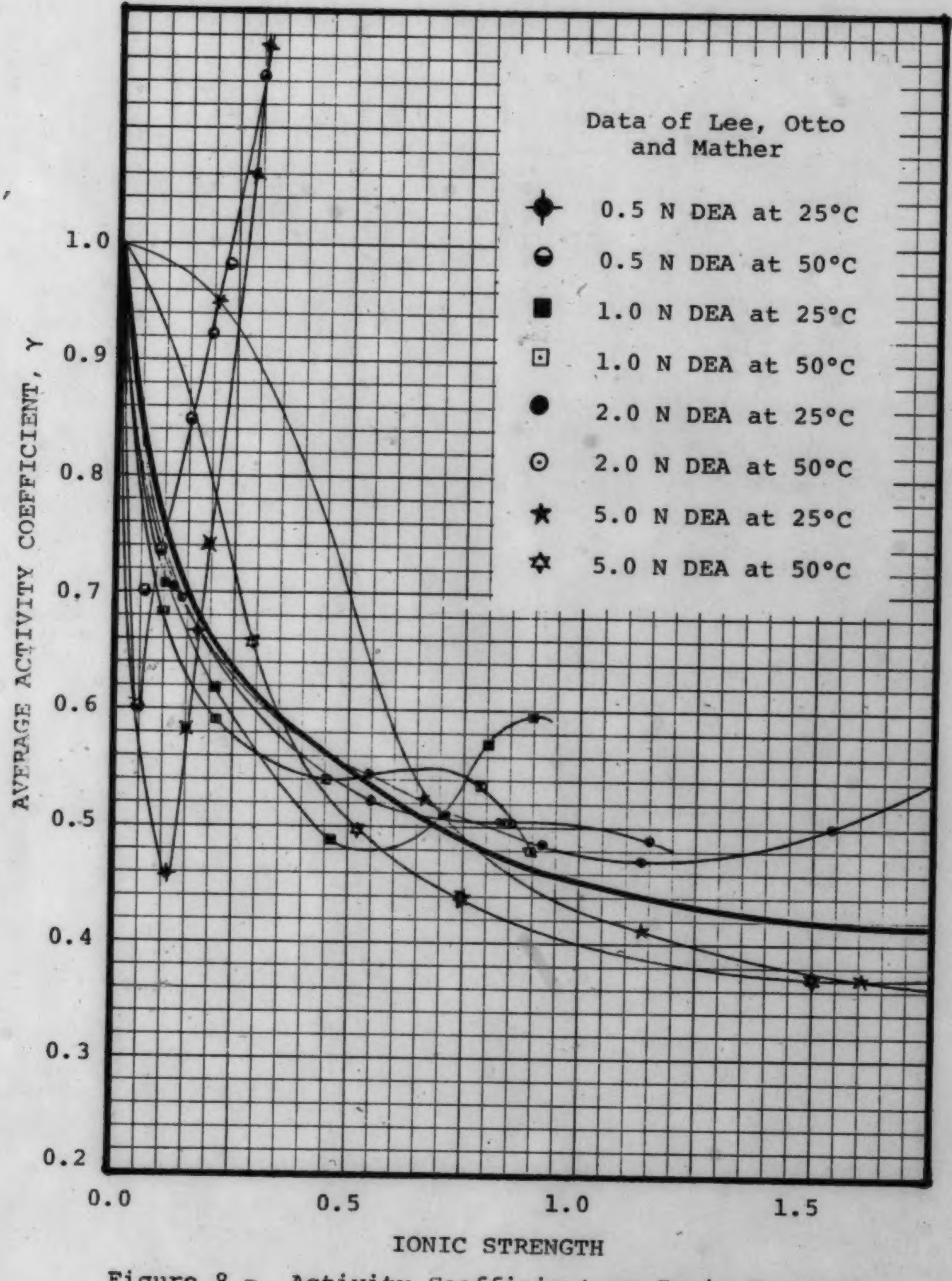


Figure 8 - Activity Coefficient vs Ionic Strength

$\gamma = f_1\ (\mu) \qquad (X_{H_2S} + X_{CO_2}) < 0.2$ moles/mole of EA

where:

μ = ionic strength

T = temperature

m = initial EA concentation.

The expressions for f_1 and f_2 are given in Appendix G. It was observed that the prediction of experimental data was not satisfactory with the empirical function, when X_{CO_2} plus X_{H_2S} was less than 0.2 moles/mole of EA. The reason for this is that the behavior of partial pressures of H_2S and CO_2 is quite different at these low loadings of acid gases. Also the partial pressure of H_2S does not follow the same trend as the partial pressure of CO_2 at these conditions. For this reason, empirical functions of temperature and initial EA concentration were added to the expressions for predicting P_{CO_2} and P_{H_2S} rather than to the expression for γ. The empirical functions are presented in Appendix G.

C. The Correlation Based on Kent and Eisenberg[10] Model:

Kent and Eisenberg[10] have used the following set of chemical equations to describe the H_2S-water-EA system:

$$RR'NH_2^+ \overset{K_1}{\rightleftharpoons} H^+ + RR'NH \qquad \text{----------} \quad (1)$$

$$H_2O \overset{K_4}{\rightleftharpoons} H^+ + OH^- \qquad \text{----------} \quad (4)$$

$$H_2S \overset{K_6}{\rightleftharpoons} H^+ + HS^- \qquad \text{----------- (6)}$$

$$HS^- \overset{K_7}{\rightleftharpoons} H^+ + S^{2-} \qquad \text{----------- (7)}$$

$$P_{H_2S} = H_{H_2S}[H_2S] \qquad \text{----------- (9)}$$

To describe the CO_2-water-EA system the equations used are:

$$RR'NH_2^+ \overset{K_1}{\rightleftharpoons} H^+ + RR'NH \qquad \text{----------- (1)}$$

$$RR'NCO\bar{O} \overset{K_2}{\rightleftharpoons} RR'NH + HCO_3^- \qquad \text{----------- (2)}$$

$$H_2O+CO_2 \overset{K_3}{\rightleftharpoons} H^+ + HCO_3^- \qquad \text{----------- (3)}$$

$$H_2O \overset{K_4}{\rightleftharpoons} H^+ + OH^- \qquad \text{----------- (4)}$$

$$HCO_3^- \overset{K_5}{\rightleftharpoons} H^+ + CO_3^{2-} \qquad \text{----------- (5)}$$

$$P_{CO_2} = H_{CO_2}[CO_2] \qquad \text{----------- (8)}$$

RR'NH represents ethanolamine, where R stands for C_2H_4OH and R' for H, for MEA; and R and R' stand for C_2H_4OH for DEA.

The second set of equations (for CO_2-water-EA system) is similar to that proposed by Danckwerts and McNeil[4]. Values of equilibrium constants for all the above equations have been published[10]. However, if the first set of equations is solved for H_2S-water-EA system to predict P_{H_2S} using the published equilibrium constants, an unsatisfactory fit of the published vapor data results[10]. Similarly if the second set of equations for CO_2-water-EA system is solved for P_{CO_2} an unsatisfactory fit of the experimental data results. To solve this problem, Kent and Eisenberg[10], treated the equilibrium constant K_1, representing the EA reaction (for the system H_2S-water-EA), as a variable and accepted all the remaining equilibrium constants as published. Using published vapor pressure data for 15.3 weight percent MEA solution and 20.5 weight percent DEA solution, those values for K_1 which fit the data were found for each temperature. For CO_2-water-EA system an additional equilibrium constant, K_2, was used because CO_2 is capable of reacting directly with either MEA or DEA to form the amine salt of a substituted carbamic acid (the carbamate ion). To solve this set of equations, only K_2 was allowed to vary. For the ionic dissociation reactions, values from the literature were used. For K_1, the value found for the H_2S-water-EA system was used. Both K_1 and K_2 show an Arrhenius dependency on temperature[10].

All the above equations were combined into a model for the mixed system, i.e. the system containing both CO_2 and H_2S in aqueous EA solution. From equations (1) to (9) the following expressions for the pseudo-equilibrium constants can be written:

$$K_1 = \frac{[H^+][RR'NH]}{[RR'NH_2^{\ +}]} \qquad \text{--------} \quad (i)$$

$$K_2 = \frac{[RR'NH][HCO_3^-]}{[RR'NCOO^-]} \qquad \text{--------} \quad (ii)$$

$$K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \qquad \text{--------} \quad (iii)$$

$$K_4 = [H^+][OH^-] \qquad \text{--------} \quad (iv)$$

$$K_5 = \frac{[H^+][CO_3^{\ 2-}]}{[HCO_3^-]} \qquad \text{--------} \quad (v)$$

$$K_6 = \frac{[H^+][HS^-]}{[H_2S]} \qquad \text{--------} \quad (vi)$$

$$K_7 = \frac{[H^+][S^{2-}]}{[HS^-]} \qquad \text{--------} \quad (vii)$$

$$H_{CO_2} = \frac{P_{CO_2}}{[CO_2]} \qquad \text{--------} \quad (viii)$$

$$H_{H_2S} = \frac{P_{H_2S}}{[H_2S]} \qquad \text{--------} \quad (ix)$$

Also the following balance equations can be written:

$$m = [RR'NH] + [RR'NH_2^{\ +}] + [RR'NCOO^-] \qquad \text{----} \quad (x)$$

$$mX_{CO_2} = [R'RNCOO^-] + [CO_2] + [HCO_3^-] + [CO_3^{\ 2-}] \qquad (xi)$$

$$mX_{H_2S} = [HS^-] + [S^{2-}] + [H_2S] \qquad \text{----} \quad (xii)$$

$$[RR'NH_2^+] + [H^+] = [HCO_3^-] + [RR'NCO\bar{O}] + 2[CO_3^{2-}] + 2[S^-] + [OH^-] + [HS^-] \quad \text{-------- (xiii)}$$

where all the concentrations are in moles/liter of solution. Also m is in moles of EA/liter of solution. Equations (i) through (xiii) can be solved simultaneously to obtain expressions for calculating P_{CO_2} and P_{H_2S} when liquid composition and temperature of the system are known. These expressions can be written as:

$$P_{H_2S} = \frac{H_{H_2S}}{K_6K_7} \cdot \frac{A[H^+]^2}{\left(1 + \frac{[H^+]}{K_7}\right)} \quad \text{---------- (14)}$$

$$P_{CO_2} = \frac{H_{CO_2}}{K_3K_5} \cdot \frac{B[H^+]^2}{\left(1 + \frac{[H^+]}{K_5} + \frac{m[H^+]}{K_2K_5K'}\right)} \quad \text{---------- (15)}$$

$$[H^+] = \frac{A\left(1 + \frac{K_7}{K_7 + [H^+]}\right)}{\left(1 + \frac{m}{K_1K'}\right)} + \frac{B\left(1 + \frac{K_2K_5}{K_2K_5 + K_2[H^+] + \frac{m[H^+]}{K'}}\right)}{\left(1 + \frac{m}{K_1K'}\right)} + \frac{K_4}{[H^+]\left(1 + \frac{m}{K_1K'}\right)} \quad \text{----- (16)}$$

where

$$A = X_{H_2S}m - \frac{P_{H_2S}}{H_{H_2S}}$$

$$B = X_{CO_2}m - \frac{P_{CO_2}}{H_{CO_2}}$$

and

$$K' = 1 + \frac{[H^+]}{K_1} + \frac{P_{CO_2}\ K_3}{K_2\ H_{CO_2}[H^+]}$$

Using the values of K_1 and K_2 from the work of Kent and Eisenberg[10], and the published values for K_3 through K_7, H_{CO_2} and H_{H_2S}, equations (14) to (16) can be solved for P_{CO_2} and P_{H_2S}. The numerical method of successive approximations was found to be adequate to solve these equations.

D. Comparison of Predictive Capabilities of the Models:

The starting point, for both Klyamer et al. and Kent and Eisenberg models, is the postulation of chemical reactions occuring in the solution. It is shown in Appendix D that for the system H_2S-CO_2-water-EA only seven independent reactions are possible and that the sets of reactions postulated in the two models, though not identical in form, are chemically equivalent. The model of Klyamer et al. is more sound from a thermodynamic standpoint since it incorporates the effect of non-ideality of the liquid phase by using activity coefficients. The substitution of partial pressure by fugacity, in the modified form of this model, lends it more theoretical support at higher pressures. The inclusion of fugacity takes care of the non-ideality of the gas phase. The model of Kent and Eisenberg incorporates all the non-idealities into two parameters, namely K_1 and K_2. This changes the nature of K_1 and K_2 from equilibrium constants to two empirical parameters which enable the model to fit the experimental data better.

The following generalizations can be made about the prediction capabilities of the three models (namely, Klyamer et al., Kent and Eisenberg and Modified Klyamer et al.) by observing Figures 9 to 26 in Appendix E :

(i) In general for MEA, the model of Klyamer et al. predicts lower values of P_{H_2S} and P_{CO_2} (compared to the experimental ones), for X_{CO_2} plus X_{H_2S} greater than ca. 0.3 moles/mole of EA. For loadings lower than 0.3 moles/mole of EA, values of P_{H_2S} and P_{CO_2} higher than the experimental ones are predicted. The prediction worsens with increasing EA concentration and acid gas loadings. For DEA, the prediction of P_{H_2S} and P_{CO_2} is, in general, better than that for MEA.

(ii) Only for simple systems, i.e. systems containing either CO_2 or H_2S, the data fit obtained by Kent and Eisenberg model is fairly good. For mixtures (H_2S-CO_2-water-EA system), on the other hand, prediction of P_{CO_2} and P_{H_2S} worsens with increasing EA concentration: increasing loadings of CO_2 and H_2S; and decreasing temperature.

(iii) The modified Klyamer et al. model predicts experimental data reasonably well over most conditions of temperature and EA concentrations, when both acid gases are present. For aqueous MEA solution containing either CO_2 or H_2S, the predicted P_{H_2S} and P_{CO_2} values are, in general, higher than the experimental ones. For DEA, when X_{CO_2} or X_{H_2S} is less than 0.4 moles/mole of EA, the predicted values of P_{CO_2} and P_{H_2S} are usually slightly higher than the experimental values. However, for loadings greater than 0.4 moles (of CO_2 or H_2S)/mole of EA, the fit is reasonably good. When both X_{H_2S} and X_{CO_2} are less than 0.1 mole/mole of EA, this model reproduces the trend, followed by experimental P_{H_2S} and P_{CO_2} values, however, deviation in some regions is still present.

By comparing the predictions of each of the three models with the experimental data, the following conclusions can be drawn:

(1) For simple systems only, i.e. systems containing either CO_2 or H_2S, the model of Kent and Eisenberg reproduces the experimental data best, over most conditions of temperature, EA concentrations and acid gas loadings. For the same systems, in most cases Klyamer et al. model also gives a reasonable fit. Modified Klyamer et al. model, on the other hand, usually predicts slightly higher P_{CO_2} and P_{H_2S} values, compared to the experimental ones.

(2) For mixtures of CO_2 and H_2S in aqueous solutions, the Modified Klyamer et al. model fits the experimental data best, especially as temperature decreases; EA concentration increases; and as the loading of acid gases increases. For loadings of CO_2 plus H_2S greater than ca. 0.8 moles/mole of EA, the modified Klyamer et al. model predicts P_{CO_2} and P_{H_2S} which are slightly lower than experimental values, but are much better than predictions from the other two models. For DEA the Kent and Eisenberg model, though not better than modified model for mixtures, is better than the Klyamer et al. model in most cases. For MEA, both the Klyamer et al. and the Kent and Eisenberg, models give results which are in error by about the same order of magnitude. Tables I and II, summarize the above observations for the mixtures of CO_2 and H_2S in EA solutions. Each entry in the table gives the percent deviation

in the predicted partial pressure values as compared to the experimental ones. Models I, II, and III stand for Klyamer et al., Kent and Eisenberg and Modified Klyamer et al. models, respectively.

(3) Only the Modified Klyamer et al. model is able to reproduce the trend of sharply declining P_{H_2S} and P_{CO_2} for low acid gas loadings (when both X_{CO_2} and X_{H_2S} are less than 0.1 moles/mole of EA).

TABLE I: PERCENT DEVIATION*** IN PREDICTION OF PARTIAL PRESSURES*

AMINE	AMINE CONCENTRATIONS	PARTIAL PRESSURES	% DEVIATION					
			100 °C			40 °C		
			MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
MEA	2.5 N	P_{H_2S}	-70	-50	-15	-100	-90	+7
		P_{CO_2}	-7	-10	+27	-40	-90	+30
	5.0 N	P_{H_2S}	-120	-130	-48	-90	-140	-4
		P_{CO_2}	-100	-190	-53	-13	-130	+23
DEA			100 °C			50 °C		
			MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
	2.0 N	P_{H_2S}	-9	0	+20	-94	-35	0
		P_{CO_2}	-20	-12	+3	-124	-83	-14
	3.5 N	P_{H_2S}	-18	-13	+19	-67	-26	+20
		P_{CO_2}	-80	-80	-34	-65	-50	+19

*** Percent Deviation $\equiv \frac{(P)_{Predicted} - (P)_{Experimental}}{(P)_{Predicted}} \times 100$

* $X_{H_2S} = X_{CO_2} = 0.4$ moles/mole of EA

TABLE II: PERCENT DEVIATION IN PREDICTION OF PARTIAL PRESSURES*

AMINE	AMINE CONCENTRATIONS	PARTIAL PRESSURES	% DEVIATION					
			100 °C			40 °C		
			MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
MEA	2.5 N	P_{H_2S}	-13	-25	+10	-11	-31	+10
		P_{CO_2}	-7	-35	+27	**	**	**
	5.0 N	P_{H_2S}	-80	-80	-27	-14	-36	+14
		P_{CO_2}	-38	-67	0	**	**	**
DEA			100 °C			50 °C		
			MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
	2.0 N	P_{H_2S}	-6	0	+13	-14	0	+22
		P_{CO_2}	-9	+6	+10	-26	-31	+8
	3.5 N	P_{H_2S}	0	+15	+21	-34	0	+17
		P_{CO_2}	-62	-13	-23	-61	-31	0

** No experimental data available

* $X_{H_2S} = X_{CO_2} = 0.2$ moles/mole of EA

SUMMARY AND CONCLUSIONS

1. An experimental apparatus was designed and constructed to determine very low partial pressures of CO_2 and H_2S at high temperatures.

2. The apparatus was tested by reproducing some solubility data of H_2S and CO_2 in 2.5 N MEA at 100°C. A good agreement between this data and that in the literature, confirmed the reliability of this apparatus.

3. For pure CO_2 in 2.5 N MEA, two isotherms at 80° and 100°C were extended to very low loadings (ca. 0.02 moles/mole of MEA). Similarly, for pure H_2S in 2.5 N MEA the 80° and 100°C isotherms were extended to regions of very low H_2S partial pressures. (about 0.0004 psia)

4. Measurements were also made for mixtures of CO_2 and H_2S in 5 N MEA at 100°C. The loading of each CO_2 and H_2S was less than ca. 0.1 moles/mole of MEA. No previous data were available for this region.

5. Of the two theoretical models proposed by Klyamer et al. and Kent and Eisenberg, the former is more sound from a thermodynamic standpoint since it incorporates the effect of non-ideality of the liquid phase by using activity coefficients.

6. The modified Klyamer et al. model, reproduces the experimental data obtained in this work, as well as that from the literature, better than either original Klyamer et al. model or that of Kent and Eisenberg. (Figures 25 and 26).

7. For the case of simple systems, i.e. aqueous - EA systems containing either CO_2 or H_2S, the model of Kent and Eisenberg gives the best fit of experimental data.

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APPENDIX A

CALCULATION OF P_{H_2S}, P_{CO_2}, ETHANOLAMINE NORMALITY, X_{H_2S} and X_{CO_2}.

Calculations

a) Gas Phase:

Peak area for each gas, N_2, CO_2 and H_2S was divided by its Relative Molar Response (RMR) factor. Mole percent of each acid gas was obtained by the formula:

Mole percent H_2S =

$$\frac{\dfrac{\text{Peak Area } H_2S}{(\text{RMR})_{H_2S}} \times 100}{\dfrac{\text{Peak Area } H_2S}{(\text{RMR})_{H_2S}} + \dfrac{\text{Peak Area } CO_2}{(\text{RMR})_{CO_2}} + \dfrac{\text{Peak Area } N_2}{(\text{RMR})_{N_2}}}$$

Similarly,

Mole percent CO_2 =

$$\frac{\dfrac{\text{Peak Area } CO_2}{(\text{RMR})_{H_2S}} \times 100}{\dfrac{\text{Peak Area } H_2S}{(\text{RMR})_{H_2S}} + \dfrac{\text{Peak Area } CO_2}{(\text{RMR})_{CO_2}} + \dfrac{\text{Peak Area } N_2}{(\text{RMR})_{N_2}}}$$

RMR factors were obtained from the literature[30]. RMR for compound *i* is defined as:

$$(\text{RMR})_i = \frac{\text{Peak area of i}}{\text{mole percent of i}} \times \frac{\text{mole percent } \phi}{\text{Peak area of } \phi} \times 100$$

where ϕ refers to the internal standard (benzene) and the factor 100 represents the RMR of benzene arbitrarily assigned a response of 100 units per mole[30].

Since the total pressure was always near atmospheric and since the temperature was reasonably high, an ideal gas phase was assumed in calculating the partial pressures of H_2S and CO_2. Vapor pressure of water plus amine was subtracted from the absolute pressure in B-3 to obtain the pressure due to N_2, CO_2 and H_2S, designated as

$$\bar{P}(N_2 + H_2S + CO_2).$$

Then:

Partial Pressure of H_2S, P_{H_2S}

$$= \frac{\text{Mole percent } H_2S}{100} \times \bar{P}(N_2 + CO_2 + H_2S)$$

Similarly,

= Partial Pressure of CO_2, P_{CO_2}

$$= \frac{\text{Mole percent } CO_2}{100} \times \bar{P}(N_2 + CO_2 + H_2S)$$

b) Liquid Phase:

Normality of amine (MEA), N_{MEA}:

$$N_{MEA} = \frac{\text{ml. of sulphuric acid used x normality of the acid}}{\text{ml. of sample used}}$$

Moles CO_2 per mole of amine, X_{CO_2}:

$$X_{CO_2} = \frac{\text{ml. of hydrochloric acid used to titrate } BaCO_3 \times \text{normality of HCl}}{2 \times N_{MEA} \times \text{ml. of sample used}}$$

Moles of H_2S per mole of amine, X_{H_2S}:

$$X_{H_2S} = \frac{\left(\text{Normality of Iodine} \times \text{initial ml. of } I_2 \text{ used}\right) - \text{(ml. of thiosulphate used)} \times \text{normality of } S_2O_3^{=}}{2 \times N_{MEA} \times \text{ml. of sample used}}$$

APPENDIX B

EXPERIMENTAL RAW DATA

a) Experimental Data for the Solubility of CO_2 in MEA Solutions.

b) Experimental Data for the Solubility of H_2S in MEA Solutions.

c) Solubility of H_2S-CO_2 Mixtures in 5 N MEA Solution at 100°C.

(a) Experimental Data for the Solubility of CO_2 in MEA Solutions:

(i) 2.5 N MEA Solution

T/°C	P_{CO_2} (Psia)	X_{CO_2} (moles CO_2/mole MEA)
60	0.0113	0.195
	0.012	0.194
	0.013	0.22
80	0.0017	0.031
	0.00176	0.0313
	0.0022	0.0325
	0.003	0.052
	0.0027	0.052
	0.0097	0.093
	0.0149	0.112
	0.0126	0.115
	0.028	0.158
	0.033	0.161
	0.067	0.214
	0.071	0.220
	0.072	0.217
	0.081	0.226
100	0.00017	0.0276
	0.0002	0.0275
	0.0005	0.029
	0.00053	0.031
	0.00063	0.0312
	0.00067	0.028
	0.00076	0.036
	0.00098	0.035
	0.0010	0.033
	0.0052	0.0573
	0.0135	0.080
	0.0141	0.082
	0.023	0.094
	0.109	0.143

(ii) 5.0 N MEA Solution

T/°C	P_{CO_2} (Psia)	X_{CO_2} (Mole CO_2/mole MEA)
100	0.00034	0.035
	0.00053	0.0375
	0.00077	0.039
	0.0042	0.060
	0.0081	0.067
	0.016	0.076
	0.043	0.087
	0.054	0.087
	0.130	0.122
	0.190	0.148

(b) Experimental Data for the Solubility of H_2S in MEA Solutions:

(i) 2.5 N MEA Solution

T/°C	P_{H_2S} (Psia)	X_{H_2S} (Mole H_2S/mole MEA)
80	0.00483	0.028
	0.0052	0.027
	0.011	0.041
	0.011	0.042
	0.0166	0.046
	0.0172	0.0465
	0.023	0.055
	0.025	0.055
	0.05	0.066
	0.065	0.078
	0.079	0.078
	0.081	0.097
	0.085	0.089
	0.162	0.148

T/°C	P_{H_2S} (Psia)	X_{H_2S} (Mole H_2S/mole MEA)
100	0.0007	0.012
	0.0012	0.017
	0.0033	0.017
	0.0081	0.0216
	0.0164	0.0294
	0.062	0.053
	0.068	0.048
	0.062	0.053

(ii) 5.0 N MEA Solution:

100	0.00031	0.026
	0.0051	0.0344
	0.0097	0.0303
	0.0156	0.029
	0.040	0.037
	0.055	0.0435

(c) Solubility of H_2S-CO_2 Mixtures in 5.0 N MEA Solution at 100°C. (Partial Pressures in Psia; X, Mole of acid gas/mole MEA).

P_{H_2S}	P_{CO_2}	X_{H_2S}	X_{CO_2}
0.0019	0.0015	0.013	0.0405
0.0022	0.0029	0.0083	0.0475
0.0066	0.0088	0.010	0.072
0.026	0.00031	0.0264	0.009
0.047	0.0024	0.025	0.026
0.054	0.0038	0.0463	0.023
0.077	0.071	0.0133	0.096
0.085	0.097	0.013	0.119
0.097	0.0021	0.036	0.012
0.102	0.048	0.018	0.078
0.118	0.164	0.011	0.116
0.13	0.063	0.021	0.082
0.15	0.0094	0.032	0.028
0.16	0.0013	0.042	0.006
0.177	0.088	0.027	0.083
0.197	0.056	0.033	0.06
0.256	0.00354	0.053	0.012

P_{H_2S}	P_{CO_2}	X_{H_2S}	X_{CO_2}
0.305	0.175	0.022	0.14
0.44	0.002	0.06	0.004
0.46	0.13	0.035	0.199
0.47	0.028	0.053	0.038
0.490	0.123	0.046	0.092
0.557	0.115	0.037	0.103
0.60	0.004	0.084	0.004
0.61	0.033	0.066	0.037
0.64	0.038	0.063	0.042
0.64	0.01	0.08	0.0124
0.653	0.015	0.0796	0.02
0.716	0.0132	0.081	0.0164
0.76	0.04	0.069	0.043
0.93	0.16	0.071	0.115
0.988	0.07	0.071	0.051
1.04	0.17	0.069	0.116
1.056	0.069	0.083	0.057
1.11	0.006	0.119	0.006
1.29	0.0082	0.128	0.006
1.35	0.43	0.064	0.175

APPENDIX C

DERIVATION OF EXPRESSIONS FOR CALCULATING P_{H_2S} AND P_{CO_2} USING THE MODEL OF KLYAMER ET AL.

Derivation of Expressions for Calculating P_{H_2S} and P_{CO_2}

Using the Model of Klyamer Et Al.

$$P_{H_2S} = \frac{[H_2S]}{H_{H_2S}}$$

From equation 7, $[H_2S] = \frac{\gamma^2[HS^-][H^+]}{K_{1C}}$

Therefore,

$$P_{H_2S} = \frac{\gamma^2[HS^-][H^+]}{K_{1C}\ H_{H_2S}}$$

Neglecting $[S^{2-}]^{11,12}$, from equation 3

$$[HS^-] = mX_{H_2S} - [H_2S] = mX_{H_2S} - P_{H_2S}\ H_{H_2S} = A$$

$$P_{H_2S} = \frac{\gamma^2\ A[H^+]}{K_{1C}\ H_{H_2S}}$$

From equation 6, $[H^+] = \frac{\alpha K_w}{\gamma^2[OH^-]}$

$$P_{H_2S} = \frac{\alpha K_w A}{K_{1C}\ H_{H_2S}[OH^-]} \qquad \text{---------- (I)}$$

Neglecting $[S^{2-}]$ and $[H^+]^{11,12}$, equation 1 reduces to:

$$[RNH_3^+] = [HCO_3^-] + [RNHCO\bar{O}] + 2[CO_3^{2-}] + [OH^-] + [HS^-]$$

or

$$[RNH_3^+] = mX_{CO_2} - P_{CO_2}\,H_{CO_2} + A + [CO_3^{2-}] + [OH^-]$$

$$= B + A + [CO_3^{2-}] + [OH^-] \qquad \text{----------} \; (i)$$

substituting $[RNH_3^+]$ from equation 5 into equation (i)

$$\frac{K_i a\alpha^2 [RNH_2]}{\gamma^2 [OH^-]} = A + B + [CO_3^{2-}] + [OH^-] \qquad \text{-------} \; (ii)$$

substituting for $[RNH_2]$ from equation 4 and simplifying for $[RNH_3^+]$,

$$[RNH_3^+] = \frac{K_i a\alpha^2 (m-z)}{\{\gamma^2 [OH^-] + K_i a\alpha^2\}} = (A + B) + [CO_3^{2-}] + [OH^-]$$

$[CO_3^{2-}]$ and $[OH^-]$ are considered when X_{CO_2} is less than 0.01 moles/mole of EA.

From the above equation;

$$[OH^-] = \frac{K_i a\alpha^2 (m-z-A-B)}{\gamma^2 (A + B)} \qquad \text{----------} \; (iii)$$

substituting (iii), into equation I.

$$P_{H_2S} = \frac{K_w}{K_{1C}\, K_i\, H_{H_2S}} \cdot \frac{\gamma^2}{a\alpha} \cdot \frac{A(A + B)}{(m-z-A-B)}$$

From equation 10,

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot z \cdot \frac{[RNH_3^+]}{[RNH_2]^2}$$

$$= \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot z \cdot \frac{K_i\ a\alpha^2}{\gamma^2[OH^-][RNH_2]} \qquad \text{---------- (II)}$$

From equation 4,

$$[RNH_2] = m - z - [RNH_3^+] = m-z-A-B \qquad \text{-------- (iv)}$$

substituting (iii) and (iv) in (II):

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{a^2\alpha^2} \cdot \frac{z(A + B)}{(m-z-A-B)^2} \qquad \text{-------- (15)}$$

From equation 2,

$$[RNHCO\bar{O}] = z = mX_{CO_2} - P_{CO_2}H_{CO_2} - [HCO_3^-] - \cancel{[CO_3^{2-}]}$$

$$= B - [HCO_3^-]$$

or

$$[HCO_3^-] = (B - z) \qquad \text{---------- (v)}$$

$$[HCO_3^-] = \frac{K_{1\gamma}\ \alpha[CO_2]}{\gamma^2[H^+]} = \frac{K_{1\gamma}\ H_{CO_2}\ P_{CO_2}\ [OH^-]}{K_w}$$

substituting value of $[OH^-]$ from (iii)

$$[HCO_3^-] = \frac{K_{1\gamma}\ H_{CO_2}\ P_{CO_2}}{K_w} \cdot \frac{K_i\ a\alpha^2[RNH_2]}{\gamma^2\ (A+B)} \qquad \text{------ (vi)}$$

From equation 10,

$$\frac{1}{K_m} = \frac{a^2 \alpha^2 \, [RNH_2]^2 \, P_{CO_2}}{\gamma^2 \, [RNH_3^+] [RNHCO\bar{O}]}$$

Multiplying equation (vi) by $\dfrac{a[RNH_2]}{a[RNH_2]} \cdot \dfrac{[RNHCO\bar{O}]}{[RNHCO\bar{O}]}$ (= 1)

and rearranging,

$$[RNH_2] = \frac{K_{1Y} \, H_{CO_2} \, K_i}{K_w \, K_m} \cdot \frac{z}{a \, [HCO_3^-]}$$

$$= \frac{K_{1Y} \, H_{CO_2} \, K_i}{K_w \, K_m} \cdot \frac{z}{a \, (B-z)} \qquad \text{-------- (vii)}$$

substituting (vii) into (iv) and rearranging,

$$A = m - z - B - \frac{K_i \, K_{1Y} \, H_{CO_2}}{K_w \, K_m} \cdot \frac{z}{a \, (B-z)}$$

--------- (16)

APPENDIX D

PROOF THAT CHEMICAL EQUATIONS POSTULATED IN THE TWO THEORETICAL MODELS ARE EQUIVALENT.

PROOF THAT CHEMICAL EQUATIONS POSTULATED IN THE TWO THEORETICAL MODELS ARE EQUIVALENT

Zeggeren and Storey[32] have shown that the number of independent reactions possible for a given system is given by:

number of independent reactions

= number of species - rank of atom matrix.

For the system CO_2-H_2S-water-EA,

number of species

= 12 (RR'NH, $RR'NCO\bar{O}$, $RR'NH_2^+$, H_2O, H^+, OH^-, H_2S,

HS^-, S^{2-}, CO_2, HCO_3^-, and CO_3^{2-}).

Rank of atom matrix = 5 (N,C,H,O,S).

Therefore,

number of independent reactions = 12 - 5 = 7

Reaction - (1) of Kent and Eisenberg model is a combination of reactions (a) and (c) of Klyamer et al. model. Similarly reaction (2) of Kent and Eisenberg model is a combination of reactions (a), (c), (e) and (f) of Klyamer et al. model. Therefore, though the seven reactions postulated in the two models are different in form, they are chemically equivalent.

APPENDIX E

COMPARISONS OF PREDICTED PARTIAL PRESSURES WITH EXPERIMENTAL DATA

————————	Experimental Data*
—— --- ——	Prediction by Klyamer et al. model
—— · ——	Prediction by Kent and Eisenberg model
– – – – – –	Prediction by Modified Klyamer et al. model

* of Lee, Otto and Mather for figures 9 to 24;
of this work for figures 25 and 26.

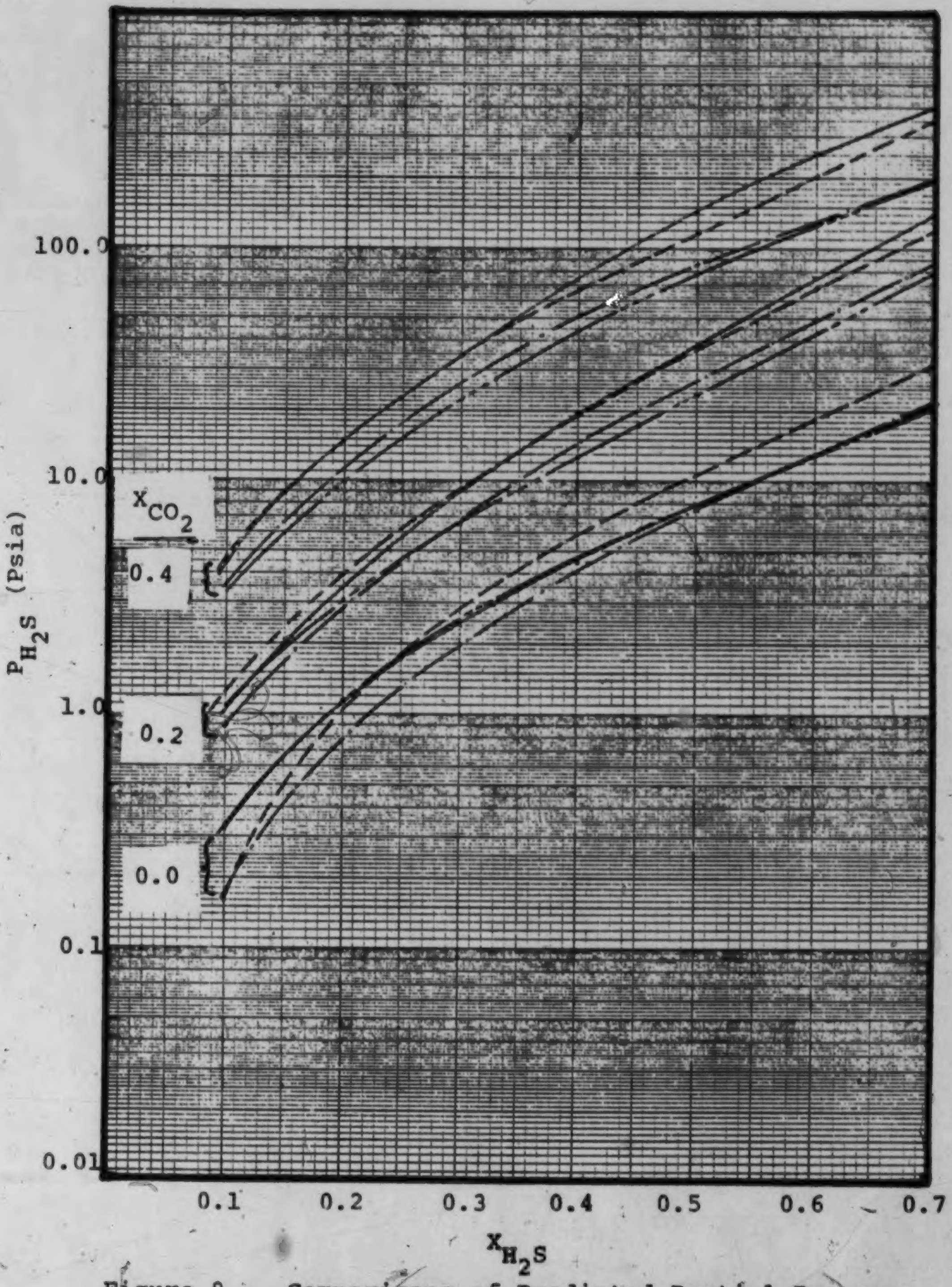

Figure 9 - Comparisons of Predicted Partial Pressure of H_2S for 2.5 N MEA at 100°C, with Published Data.

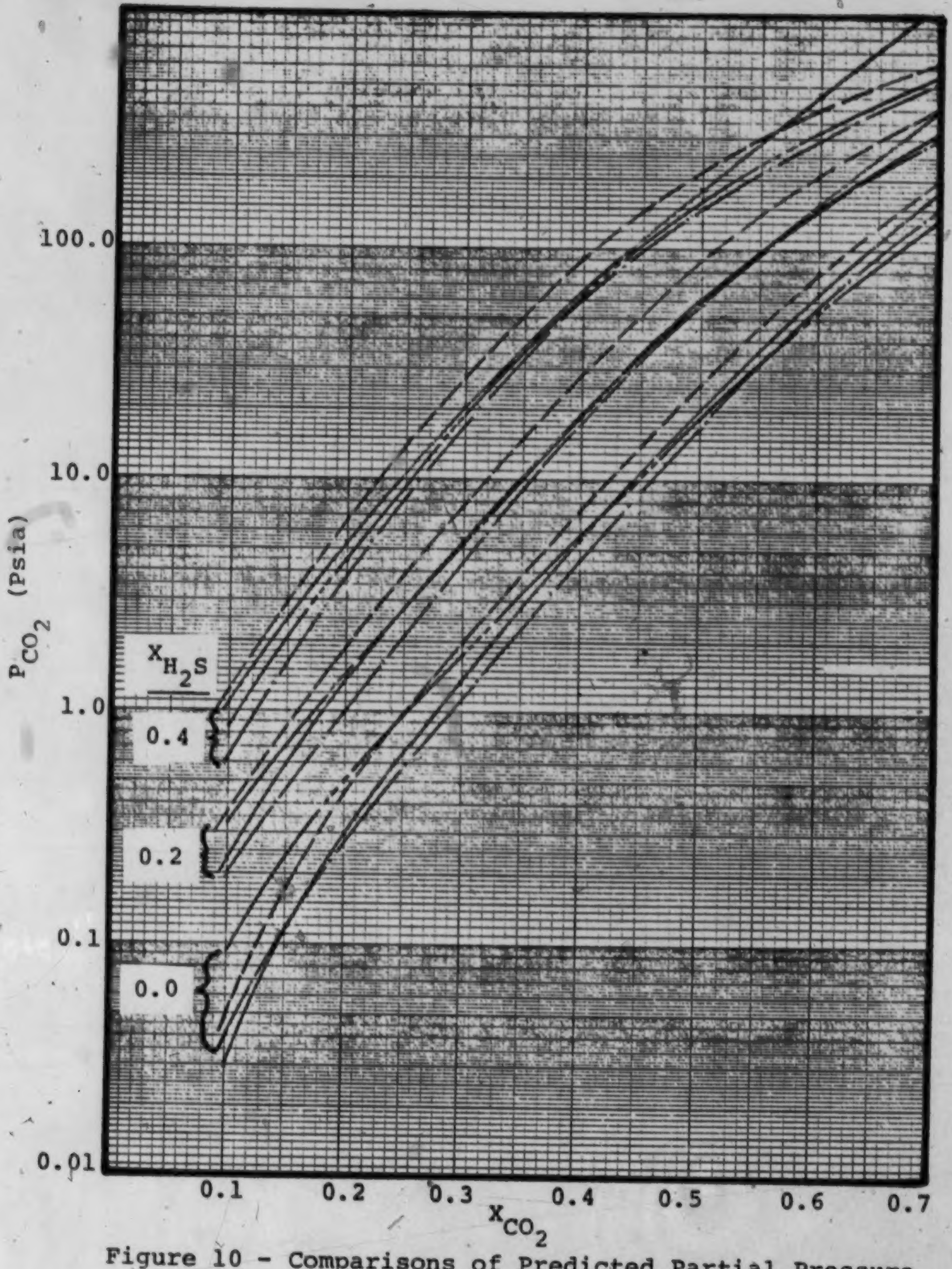

Figure 10 - Comparisons of Predicted Partial Pressure of CO_2 for 2.5 N MEA at 100°C, with Published Data.

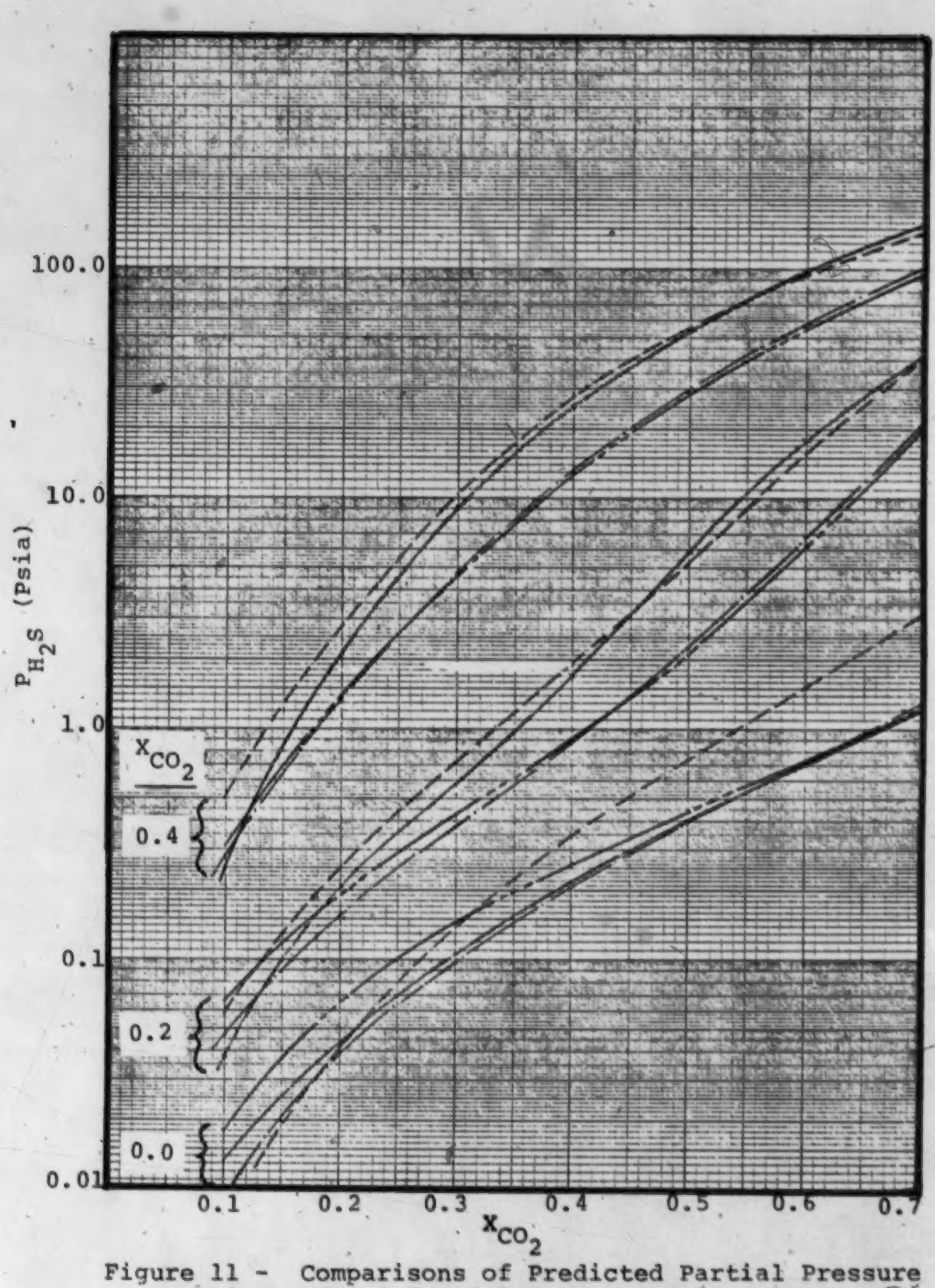

Figure 11 - Comparisons of Predicted Partial Pressure of H_2S for 2.5 N MEA at 40°C, with Published Data.

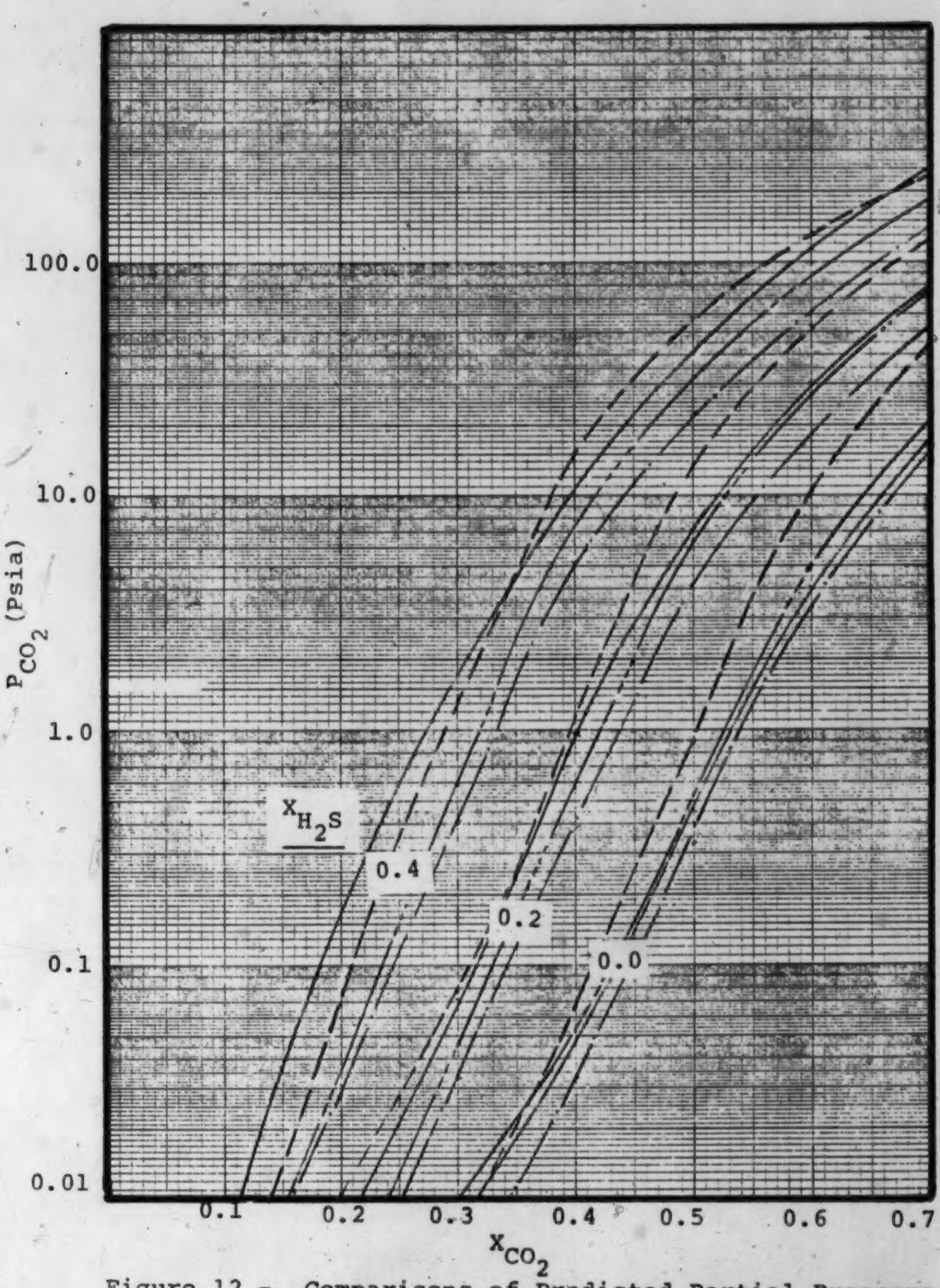

Figure 12 - Comparisons of Predicted Partial Pressure of CO_2 for 2.5 N MEA at 40°C, with Published Data.

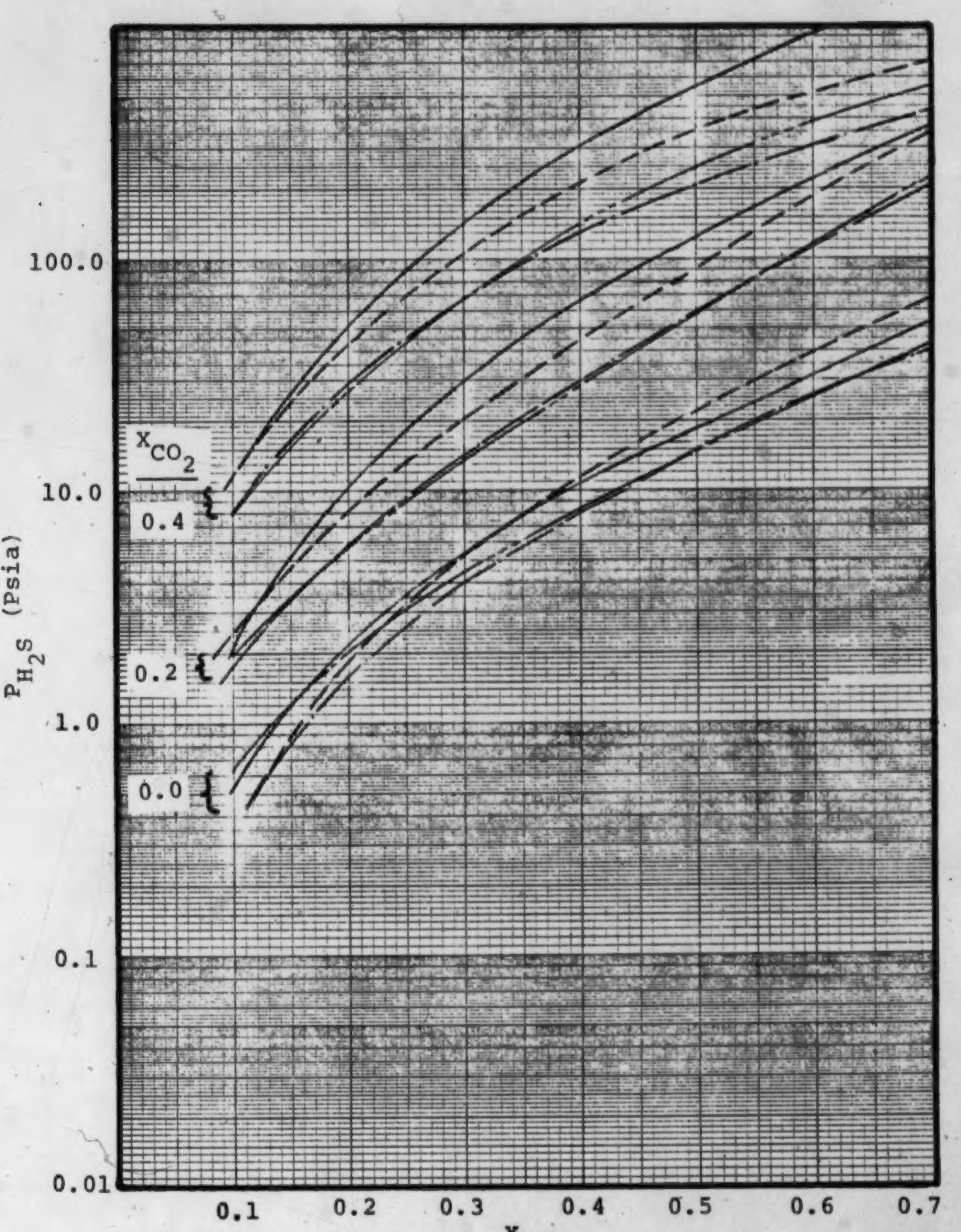

Figure 13 - Comparisons of Predicted Partial Pressure of H_2S for 5 N MEA at 100°C, with Published Data.

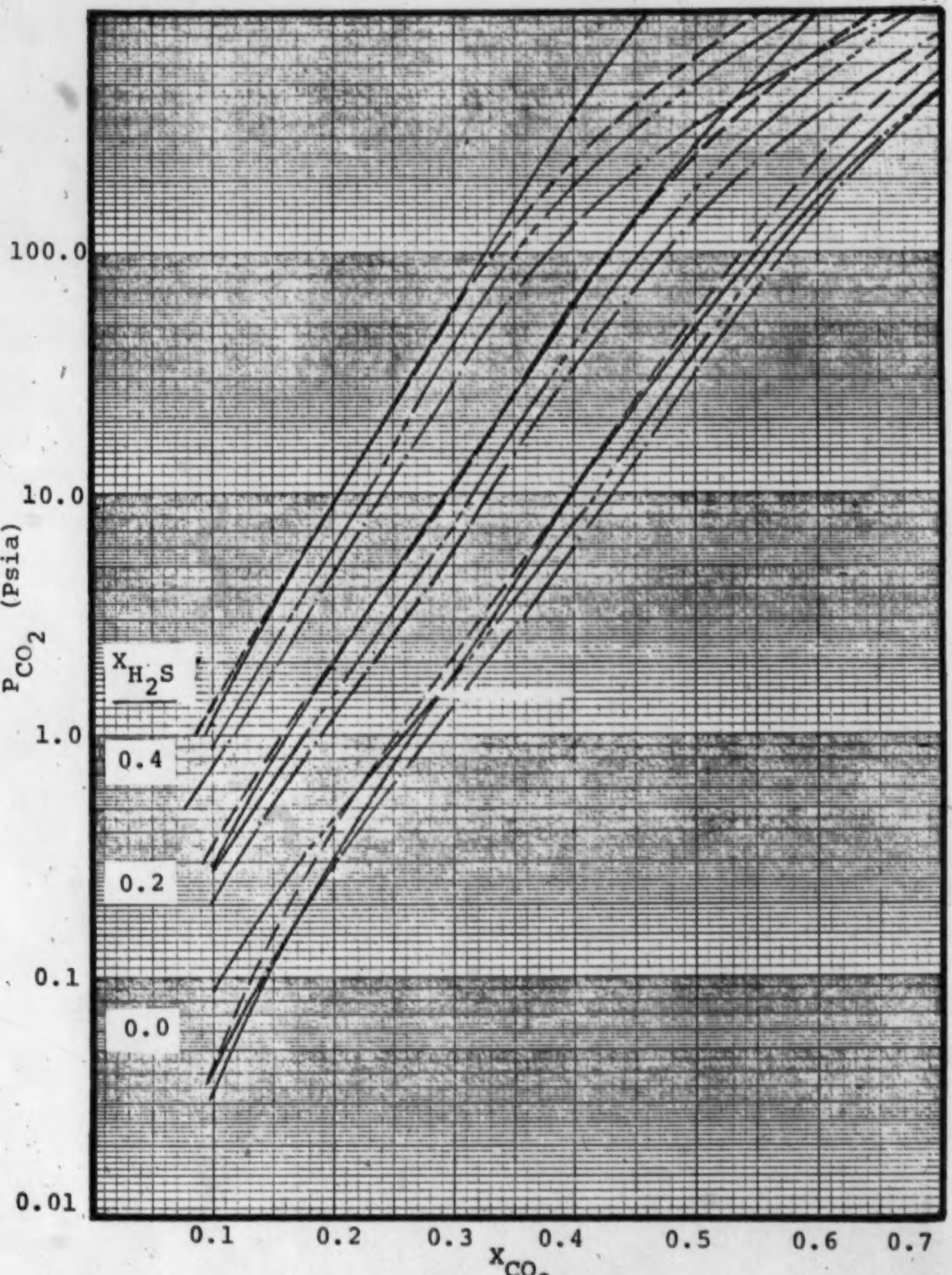

Figure 14 - Comparisons of Predicted Partial Pressure of CO_2 for 5 N MEA at 100°C, with Published Data.

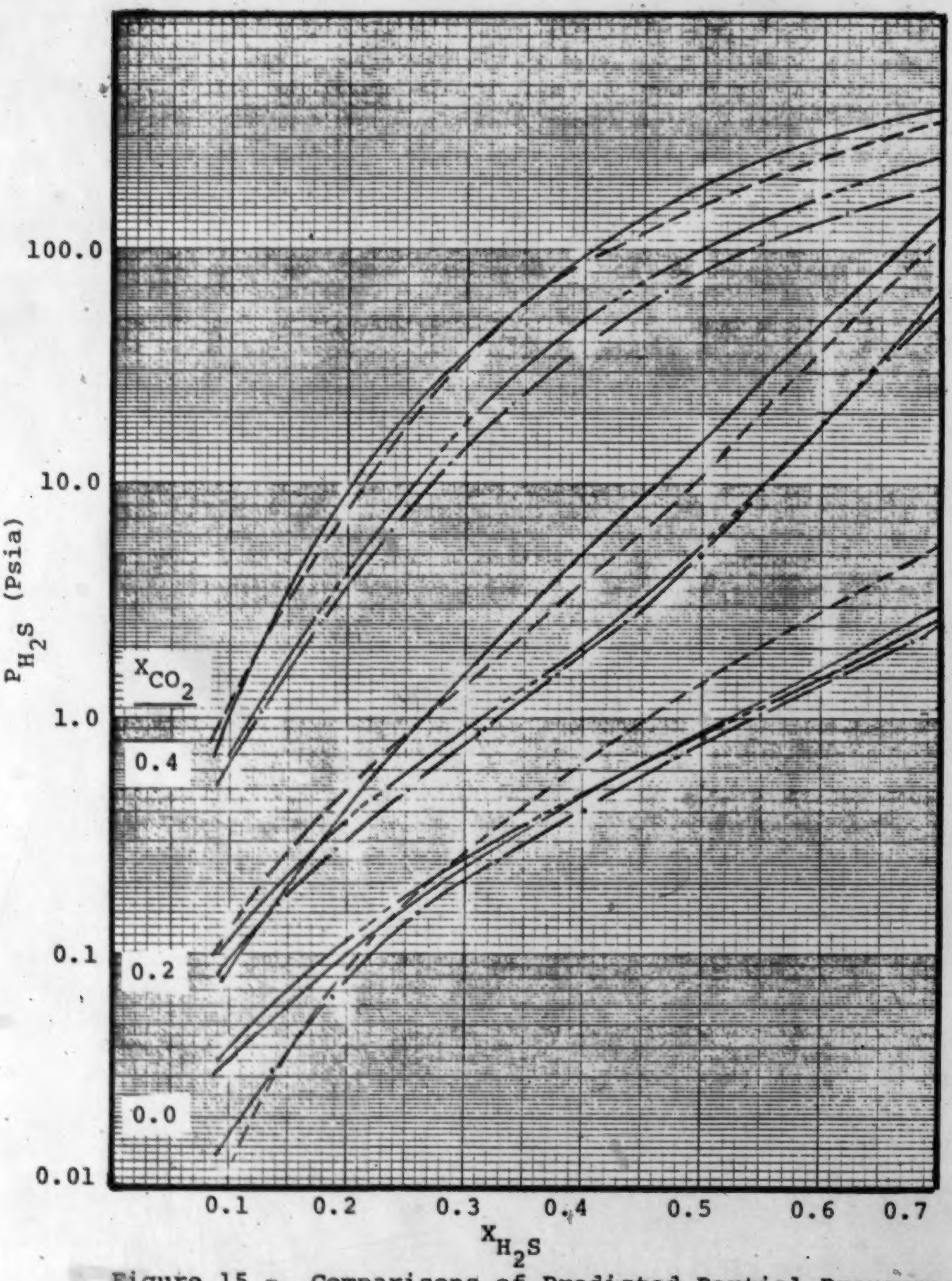

Figure 15 - Comparisons of Predicted Partial Pressure of H_2S for 5 N MEA at 40°C, with Published Data.

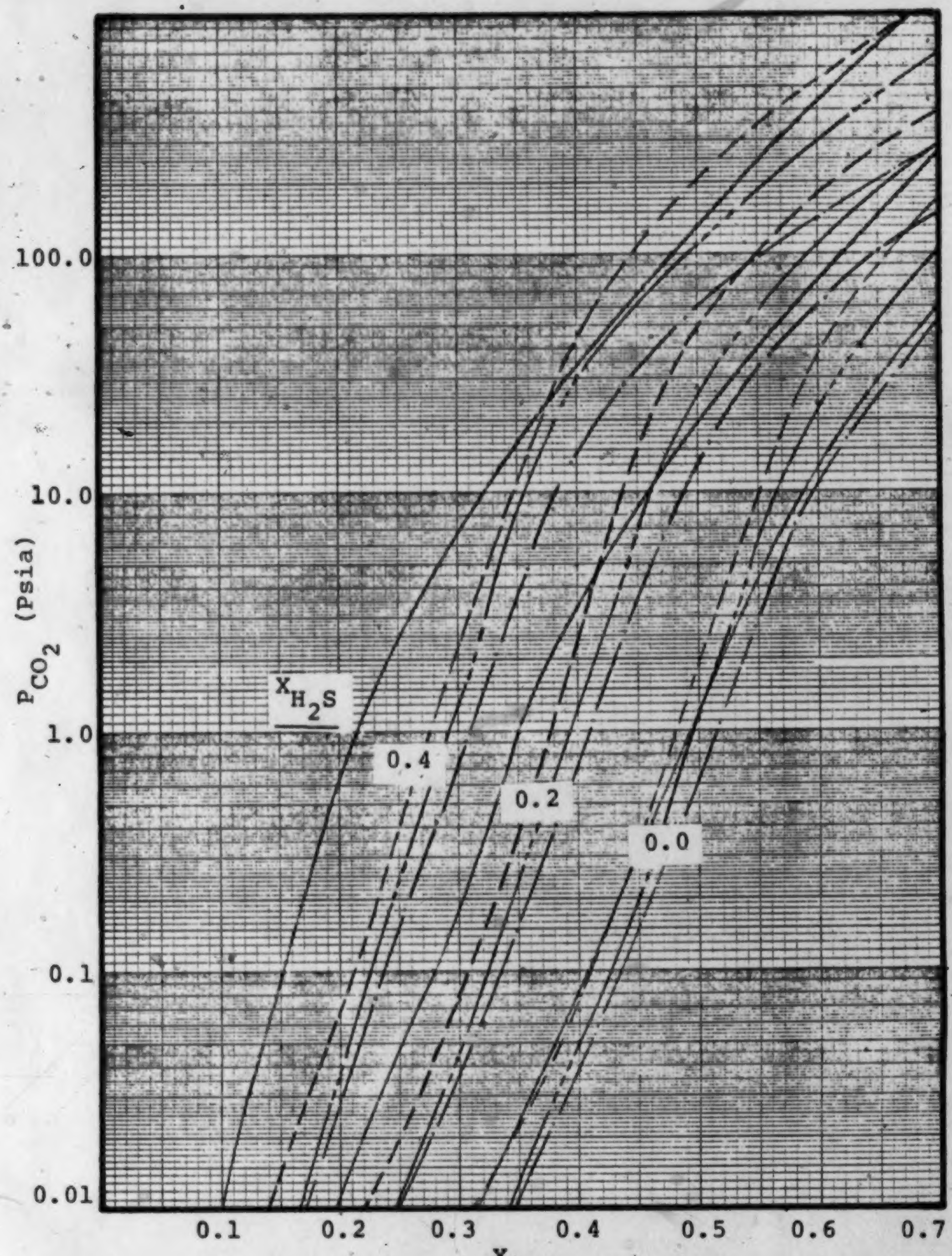

Figure 16 - Comparisons of Predicted Partial Pressure of CO_2 for 5 N MEA at 40°C, with Published Data.

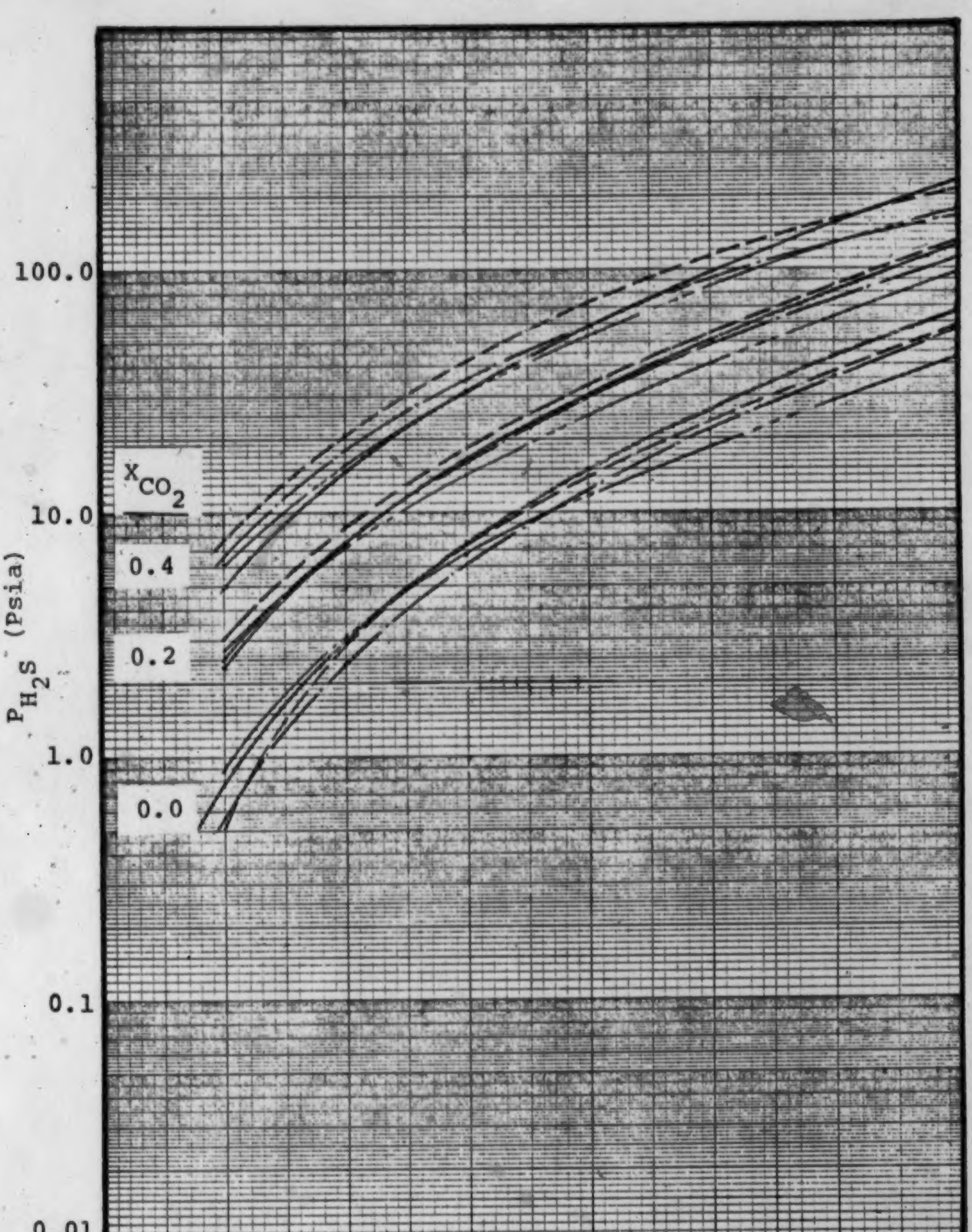

Figure 17 - Comparisons of Predicted Partial Pressure of H_2S for 2 N DEA at 100°C, with Published Data.

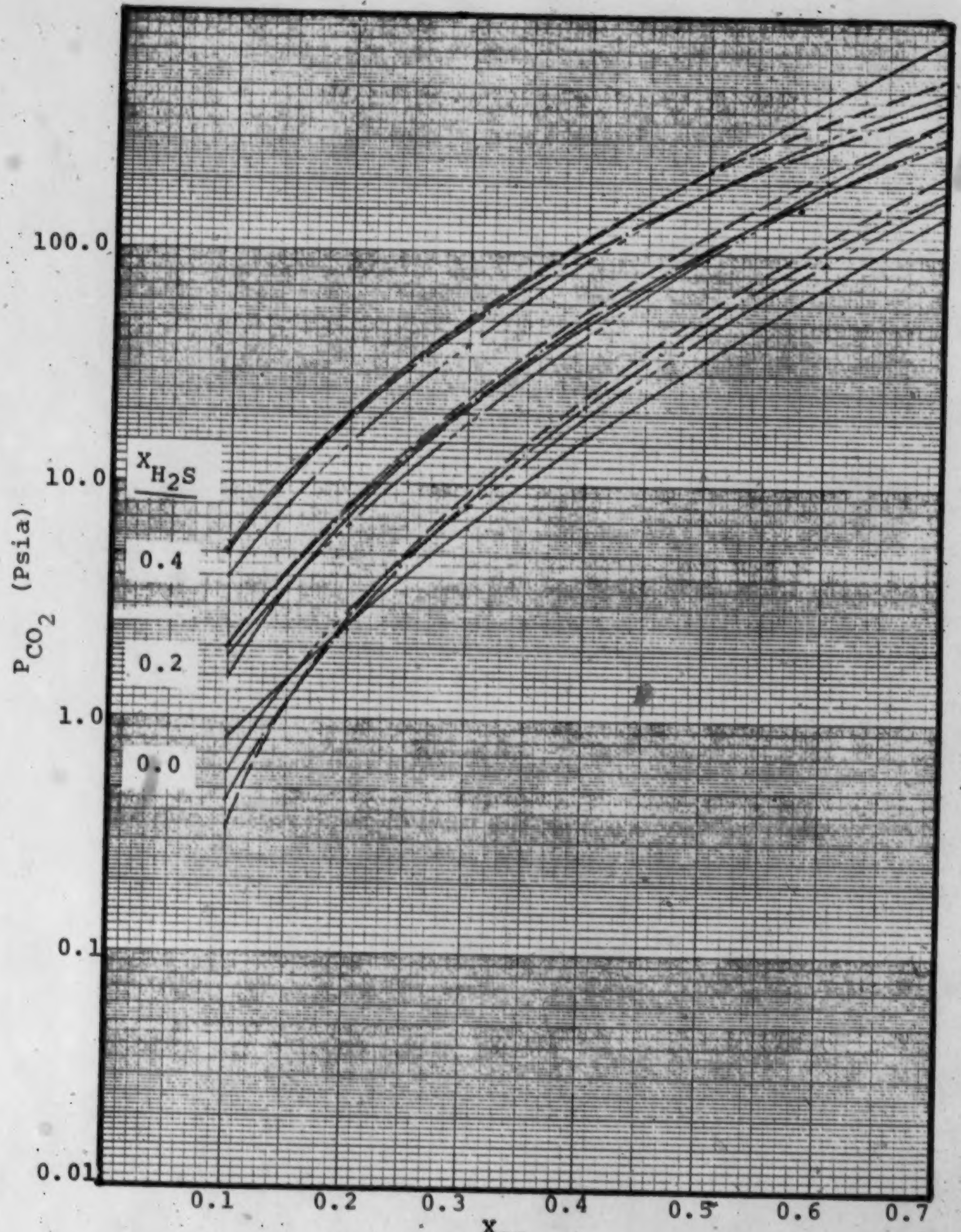

Figure 18 - Comparisons of Predicted Partial Pressure of CO_2 for 2 N DEA at 100°C, with Published Data.

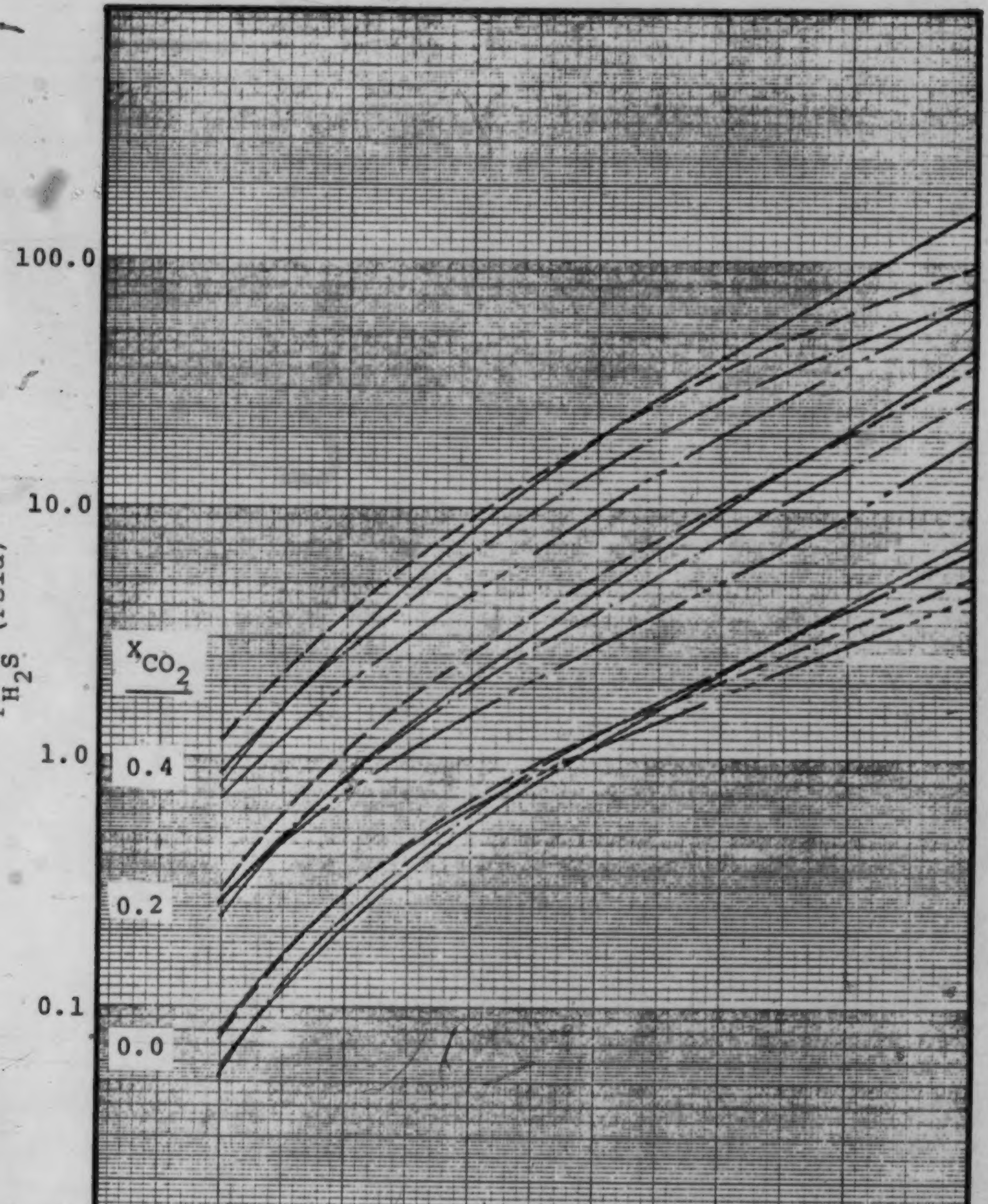

Figure 19 - Comparisons of Predicted Partial Pressure of H_2S for 2 N DEA at 50°C, with Published Data.

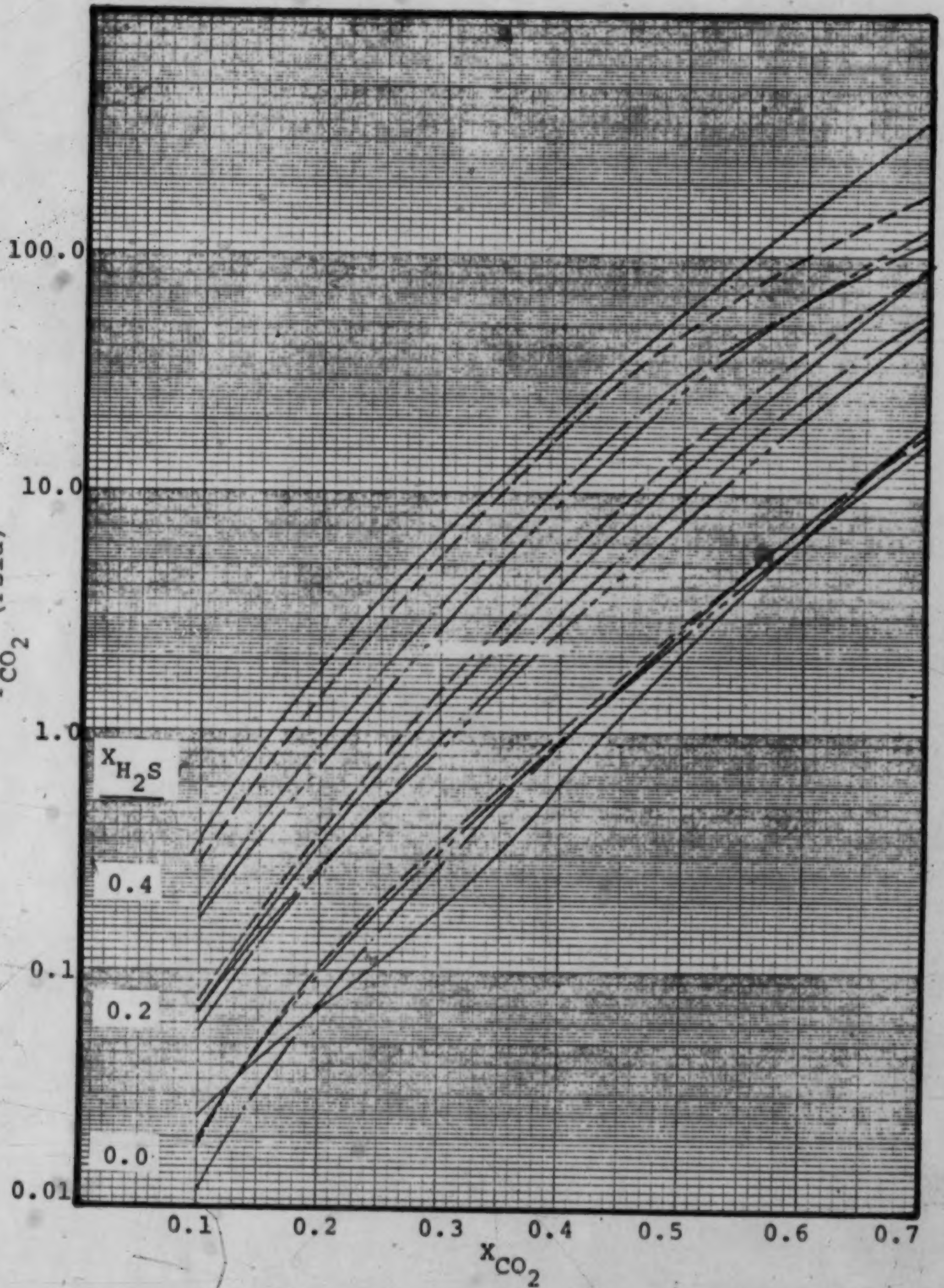

Figure 20 - Comparisons of Predicted Partial Pressure of CO_2 for 2 N DEA at 50°C, with Published Data.

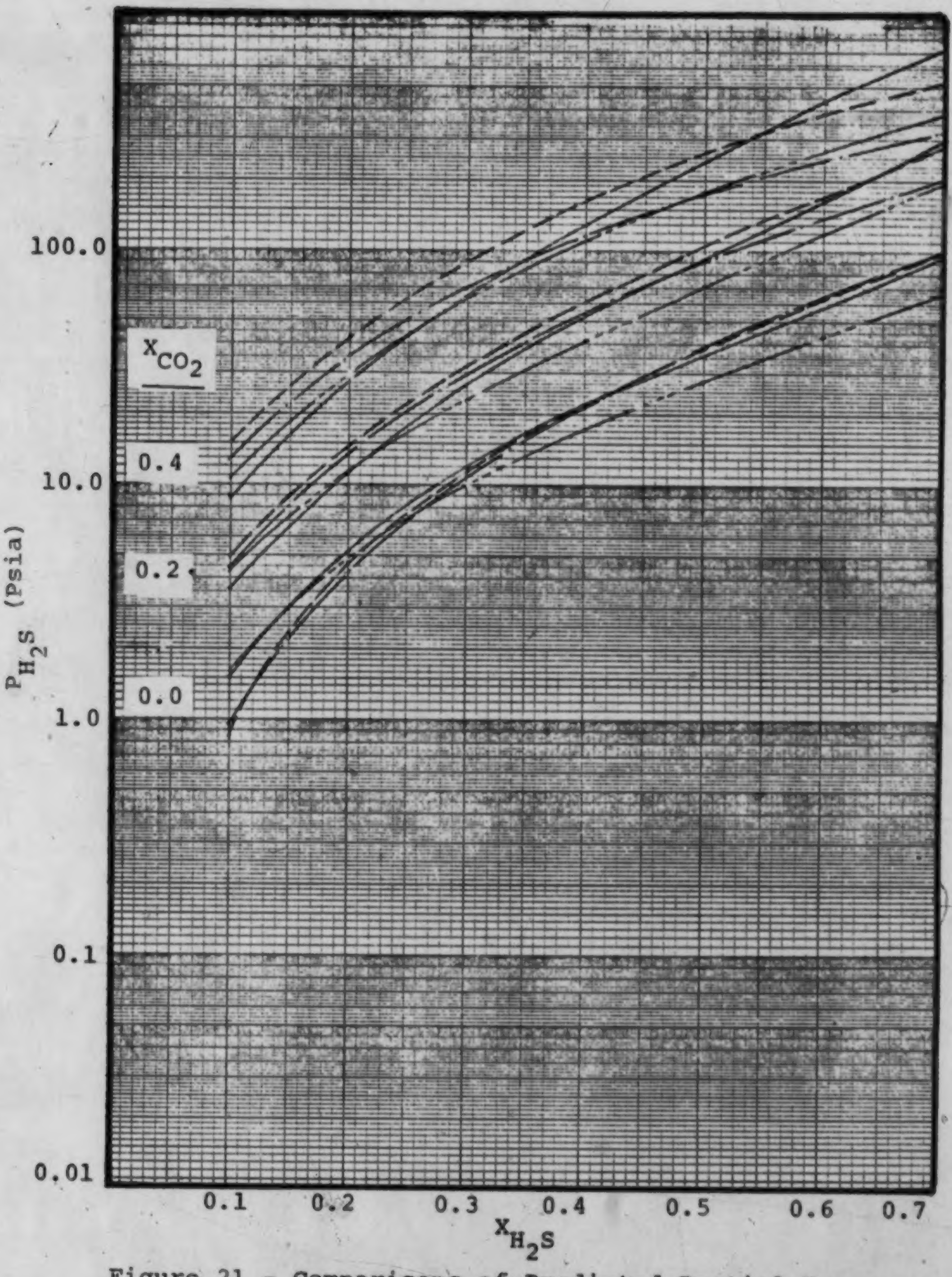

Figure 21 - Comparisons of Predicted Partial Pressure of H_2S for 3.5 N DEA at 100°C, with Published Data.

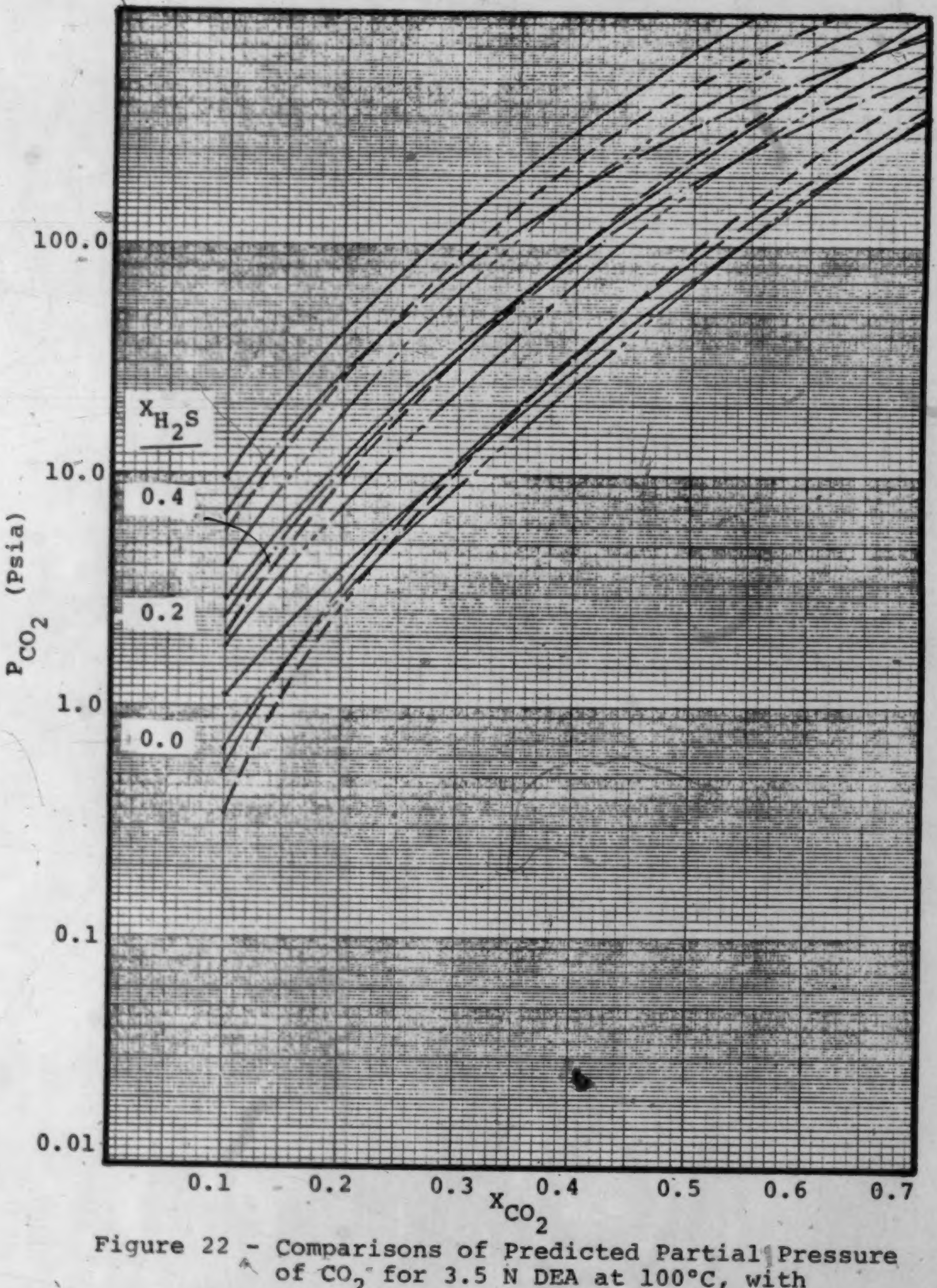

Figure 22 - Comparisons of Predicted Partial Pressure of CO_2 for 3.5 N DEA at 100°C, with Published Data.

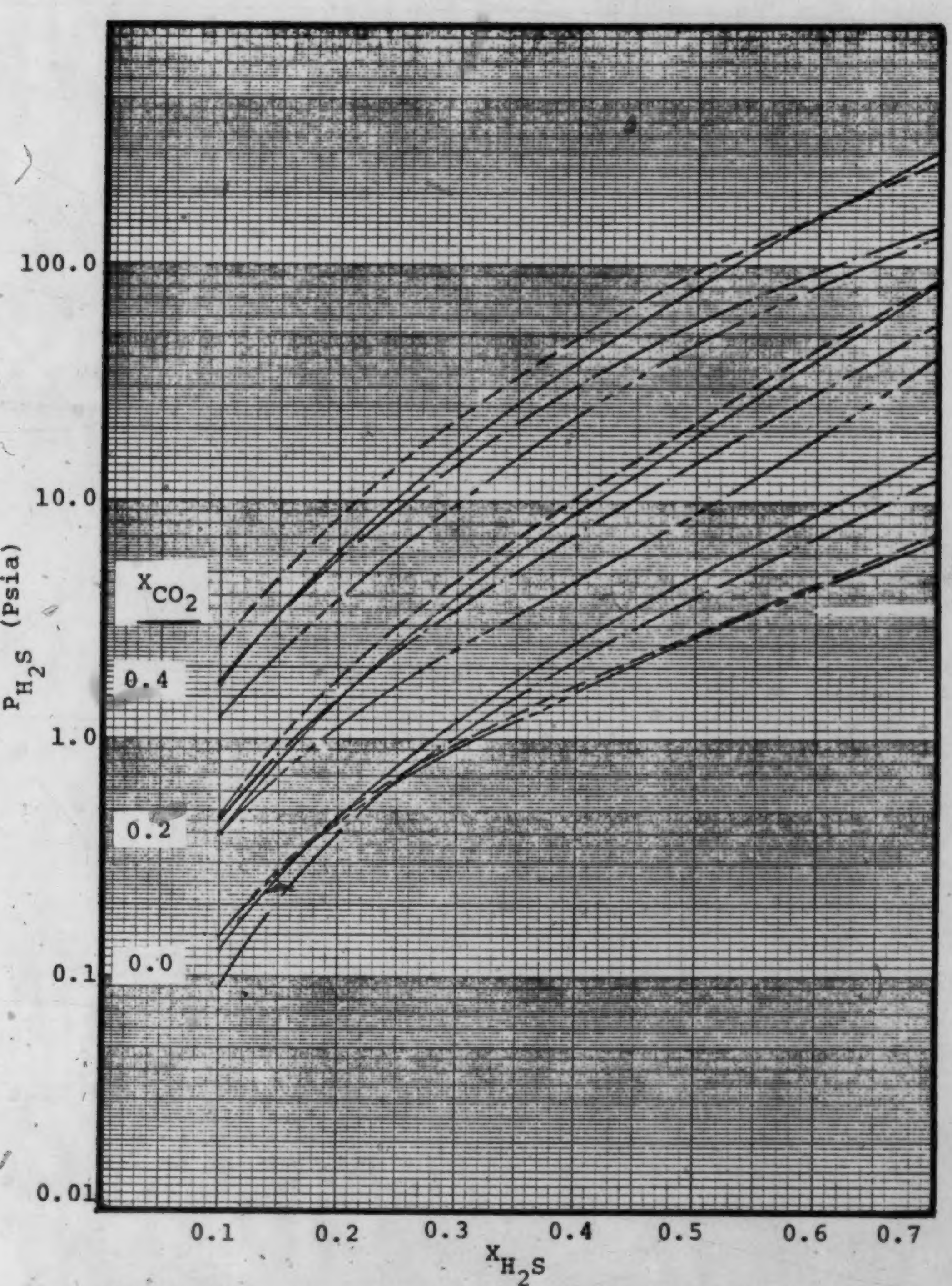

Figure 23 - Comparisons of Predicted Partial Pressure of H_2S for 3.5 N DEA at 50°C, with Published Data.

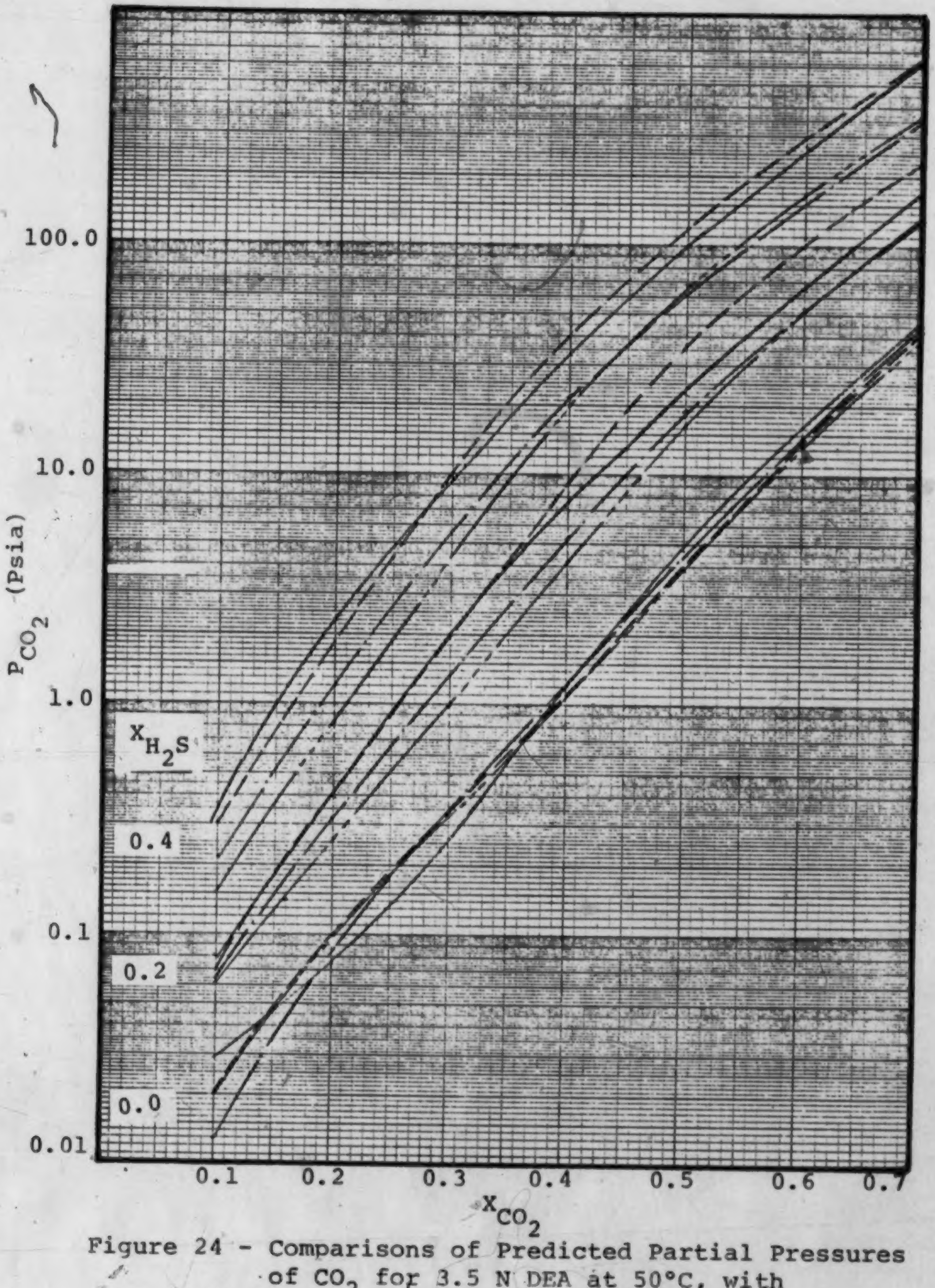

Figure 24 - Comparisons of Predicted Partial Pressures of CO_2 for 3.5 N DEA at 50°C, with Published Data.

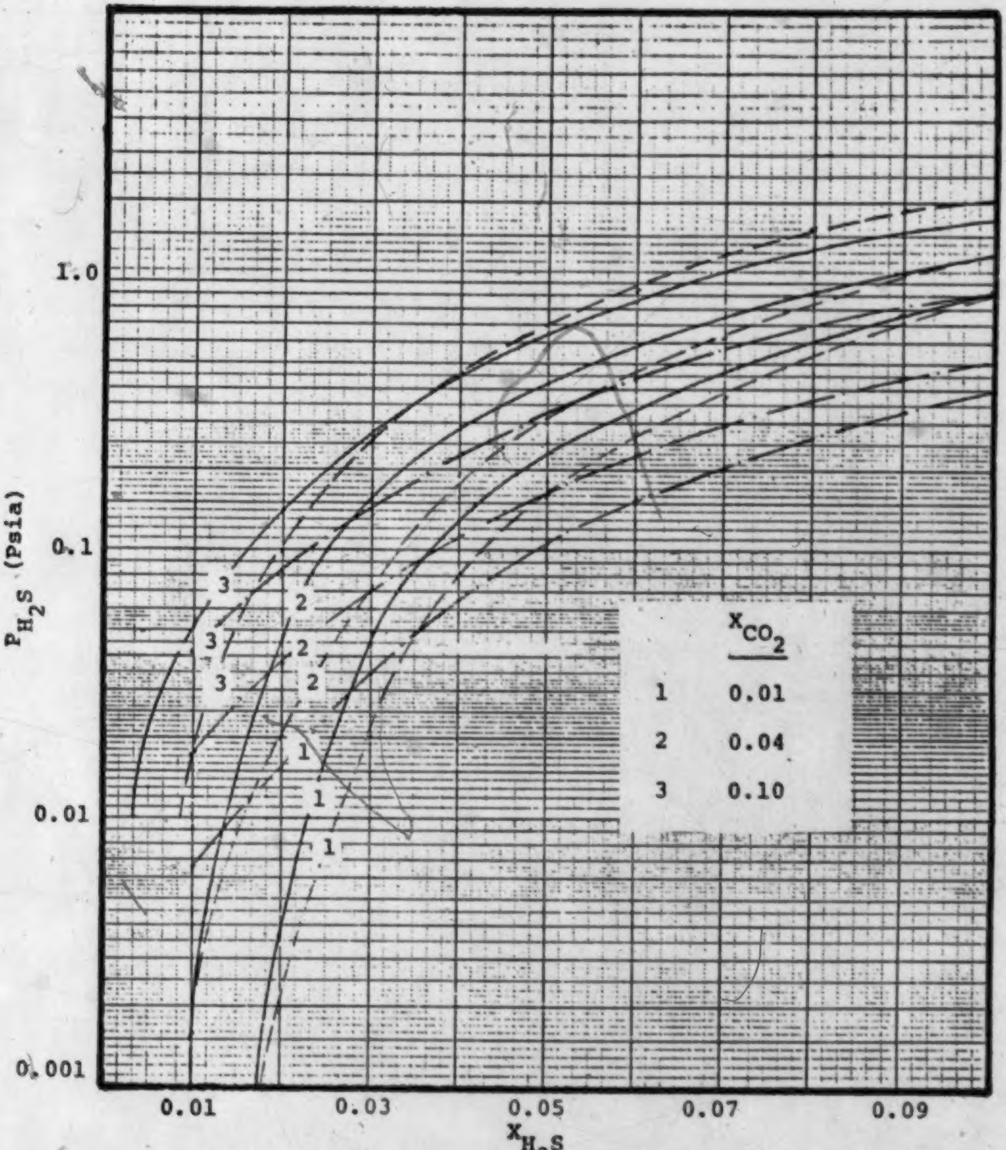

Figure 25 - Comparisons of Predicted Partial Pressure of H_2S for 5 N MEA at 100°C, with Data Obtained in This Study.

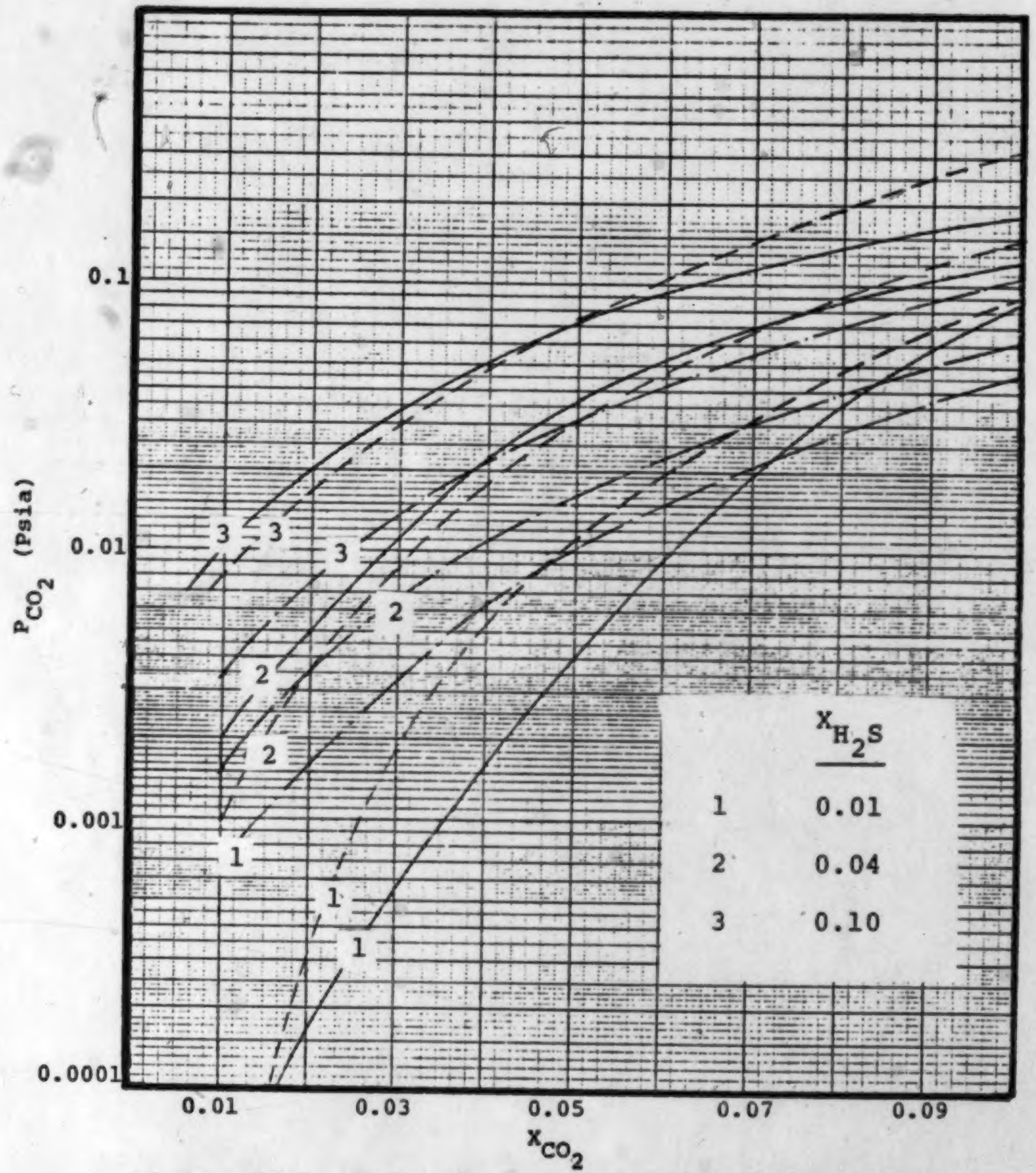

Figure 26 - Comparisons of Predicted Partial Pressure of CO_2 for 5 N MEA at 100°C, with Data Obtained in This Study.

APPENDIX F

COMPUTER PROGRAMS

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*                                                          *
* PROGRAM FOR CALCULATION OF PARTIAL PRESSURES OF H2S AND *
*  CO2 OVER ETHANOLAMINE SOLUTIONS  ----  USING MODIFIED  *
*  KLYAMER ET AL. MODEL                                   *
*                                                          *
*    INPUT VARIABLES FOR THE PROGRAM ARE ,                *
*    T - TEMPERATURE IN DEGREE KELVIN                     *
 *    MM - MOLES OF ETHANOLAMINE PER 1000.0 GRAMS OF WATER  *
*    KLMN = 1 FOR MONO-  AND 2 FOR DI-ETHANOLAMINE        *
*                                                          *
************************************************************
************************************************************
      REAL KIY,KI,KW,KIC,K2C,MA1,MA2,K1,KM,MU,MM,K2Y
      DIMENSION DD(3)
      DIMENSION Y(3),PHI(3)
      DO 101 I=1,3
      PHI(I)=0.0
  101 CONTINUE
      READ(5,1) T,MM,KLMN
 1    FORMAT(2F15.5,I1)
C     DETERMINATION OF VARIOUS PARAMETERS FOR THE ABOVE READ COND
      TT=1000.0/T
      YY=0.872446E01-0.183312E01*TT+0.33752E00*TT**2
      KIY=EXP(-2.303*YY)
      YH=-0.450823E01+0.453045E-01*T-0.580136E-04*T**2
      HH2S=EXP(-2.303*YH)
      YC=-0.248352E01+0.361175E-01*T-0.440596E-04*T**2
      HCO2=EXP(-2.303*YC)
      TW=(T-273.16)*1.8+32.0
      YW=-0.756413+0.278931E-01*TW-0.700393E-04*TW**2+0.747623E-0
      KW=EXP(2.303*(YW-15.0))
      YIC=0.110835+0.166718E-01*TW-0.684879E-04*TW**2+0.106972E-0
      KIC=EXP(2.303*(YIC-8.0))
      E2=-0.290239E04/T+7.0880-0.2379E-01*T
      K2Y=EXP(2.303*E2)
      K2C=0.1E-15
      IF(KLMN-2)2,3,3
 2    IF(0.10E04/T-2.95)4,7,7
 4    MA2=0.47424E04*(1.0/T-0.0025)-3.6341
      KM=EXP(MA2*2.303)
      GO TO 10
 7    MA1=0.458E04*(1.0/T-0.00295)-1.50
      KM=EXP(MA1*2.303)
 10   YIM=-2677.91/T-0.6169-0.4277E-03*T
      E3=EXP(2.303*YIM)
      KI=KW/E3
      AA=0.8727
      GO TO 20
 3    DA=0.36585E04*(1.0/T-0.0026)-4.0
      KM=EXP(DA*2.303)
      TTT=T-273.16
      YID=-1.609+0.41486E-01*(TTT-37.8)
      E33=EXP(YID)/0.1E09
      KI=KW/E33
      AA=0.857478+0.125767D-01*MM+0.44202D-02*MM**2
 20   GAMA=0.50
      IF(KLMN-1)21,21,22
 21   WRITE(6,221)
 221  FORMAT(1H1,/,10X,' ETHANOL AMINE PRESENT IS MEA')
      GO TO 18
 22   WRITE(6,222)
 222  FORMAT(1H1,/,10X,' ETHANOL AMINE PRESENT IS DEA')
 18   WRITE(6,399)T,MM
 399  FORMAT(//,2X,'TEMP. OF THE SYSTEM=',F7.2,//,2X,'CONC.
     1OF ETHANOL AMINE IN MOLES/1000.0 GRAM OF H2O=',F5.2)
      WRITE(6,412)HH2S,HCO2,KIY,KIC,K2Y,K2C,KW,KM,KI
 412  FORMAT(//,2X,'HENRYS CONST. FOR H2S=',E14.5,//,2X,'HEN
     1RYS CONST. FOR CO2=',E14.5,///,2X,'EQIL. CONSTANTS   K
     2IY,KIC,K2Y,K2C,KW,KM AND KI RESPECTIVELY ARE',//,2X,7E
     316.6,////)
      DO 108 LLL=2,4,2
      DO 108 II=1,10,3
      XCO2=LLL/10.0
      XH2S=II/10.0
      ALPHA=55.51/(55.51+MM*(1.0+XCO2+XH2S))
C     INITIAL VALUES OF PCO2 AND PH2S CAN BE OBTAINED USING
C     SIMPLIFIED EQUATIONS
      IF(1.0-XH2S-2.0*XCO2)68,68,67
 67   K1=(KI*KIY*HCO2)/(KM*KW)
      CQ=K1/(AA*MM)+1.0-XH2S-2.0*XCO2
      QQ=XH2S+XCO2
      HCM=SQRT((CQ/2.0)**2+(K1*XCO2)/(AA*MM))-CQ/2.0
      QT=(KW*GAMA**2*MM*XH2S*QQ)/(KI*KIC*HH2S*AA*ALPHA)
      PH2S=QT/(HCM+1.0-XH2S-2.0*XCO2)
      PCO2=(GAMA**2*XCO2*QQ)/(KM*(AA*ALPHA)**2*(HCM+1.0-XH2S
     1-2.0*XCO2)**2)
      WRITE(6,415)PCO2,PH2S
      GO TO 220
 68   A1=MM*XH2S*0.5
      B2=MM*XCO2*0.5
      IF(XH2S)416,416,417
 416  PCO2=2.0*B2/KM
      PH2S=0.0
      GO TO 418
 417  IF(XCO2)419,419,420
 419  PH2S=(KW*A1**2)/(KIC*KI*HH2S*MM)*(1.0+XH2S/0.1)
      PCO2=0.0
      GO TO 418
 420  PH2S=(KW*A1*(A1+B2))/(KIC*KI*HH2S*MM)*(2.0+XH2S/0.1)
      PCO2=2.0*(A1+B2)/KM*(1.0+XCO2/0.1)
 418  WRITE(6,415)PCO2,PH2S
 415  FORMAT(5X,E16.5)
```

```
220   Z=0.8*MM*XCO2/(1.0+4.0*XCO2)
231   ZZ=Z
      PHS=PH2S
      PCO=PCO2
      KL=0
40    A1=MM*XH2S-HH2S*PH2S
      KL=KL+1
      B2=MM*XCO2-HCO2*PCO2
      IF(A1)81,82,82
82    IF(B2)81,83,83
81    PH2S=0.95*PH2S
      PCO2=PCO2*0.95
      GO TO 231
83    FFK=MM-Z-A1-B2
      KJ=0
      IF(FFK)89,89,85
89    FFK=MM/50.0
85    HS=A1
12    RN=KI*AA*ALPHA**2
      OH=(RN*FFK)/(GAMA**2*(A1+B2))
      HPLUS=(KW*ALPHA)/(GAMA**2*OH)
      HCO3=(K1Y*ALPHA*HCO2*PCO2)/(GAMA**2*HPLUS)
      CO3=(K2Y*HCO3)/(GAMA*HPLUS)
      RNH3=(RN*(MM-Z))/(GAMA**2*OH+RN)
      S2=(K2C*HS)/(GAMA*HPLUS)
      KJ=KJ+1
      IF(KJ-10)106,106,303
106   MU=0.5*(Z+A1+HPLUS+OH+RNH3+4.0*CO3+HCO3+4.0*S2)
      ETA=GAMA
      IF(MU)300,300,301
300   MU=2.0
      GO TO 302
301   IF(MU-7.0)302,302,303
303   GAMA=0.5
      GO TO 93
302   IF(MU-0.1)74,74,75
74    GAMA=0.902308-0.199577E01*MU-0.678868E-01*(EXP(MU))+0.05
      GO TO 203
75    IF(KLMN-2)54,55,55
54    IF((XCO2+XH2S)-0.2)56,56,57
56    GAMA=0.399117-0.338402E-02*MU+0.324219E00*EXP(-MU)
      GO TO 203
57    GAMA=0.399117-0.338402E-02*MU+0.324219E00*EXP(-MU)+0.1
     15*(1.0-(0.21/(XCO2+XH2S))**0.95)+((XCO2+XH2S-0.4)/(1.0
     2+EXP(-(7.2-MM))))*(1.1-EXP(-(374.0-T)/100.0))
      GO TO 203
55    IF((XCO2+XH2S)-0.2)58,58,59
58    GAMA=0.36640-0.15975E-01*MU+0.344379E00*EXP(-MU)
      GO TO 203
59    IF(XCO2*XH2S)60,61,60
61    GAMA=0.36640-0.15975E-01*MU+0.344379E00*EXP(-MU)+(0.10
     10*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.1*((XCO2+XH2S-0.05)
     2/(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0)))*(1.05-EXP(
     3-(5.22-MM)/10.0))
      GO TO 203
60    GAMA=0.36640-0.15975E-01*MU+0.344379E00*EXP(-MU)+(0.10
     1*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.5*((XCO2+XH2S-0.30)/
     2(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0)))
203   IF(ABS((GAMA-ETA)/GAMA*100.0)-5.0)93,93,12
93    IF(XCO2)91,91,92
92    IF(XH2S)94,94,204
91    PKK=(KW*GAMA**2)/(KIC*KI*AA*ALPHA)
      PCC=SQRT(((1.0-XH2S)/2.0)**2+PKK*XH2S)
      PHS=PH2S
      PH2S=MM/(HH2S*(1.0-PKK))*(PCC-(1.0-XH2S)/2.0-PKK*XH2S)
      PCO=0.0
      GO TO 933
94    TK1=(KI*KIY*HCO2*AA*ALPHA**2)/(KW*GAMA**2)
      TK2=(KM*KW*AA)/(KI*KIY*HCO2)
      B2=MM*XCO2-PCO2*HCO2
      BB=(B2-MM/2.0-0.50/TK2)**2
      BM=MM/2.0-B2
      PCO=PCO2
      PCO2=B2/TK1*(0.50/TK2-SQRT(BB+B2/TK2)+BM)/(0.50/TK2-SQ
     1RT(BB+B2/TK2)-BM)
      B2=MM*XCO2-PCO2*HCO2
      PHS=0.0
      GO TO 933
204   FK1=(KW*GAMA**2)/(KIC*KI*HH2S*AA*ALPHA)
      FK2=(GAMA**2)/(KM*(AA*ALPHA)**2)
      FK3=(AA*KW*KM)/(KI*KIY*HCO2)
      FFK=MM-Z-A1-B2
      IF(FFK)953,953,954
953   FFK=MM/50.0
954   F1=PH2S-FK1*A1*(A1+B2)/FFK
C     NEW VALUES OF PCO2,PH2S AND Z ARE NOW OBTAINED USING
C     MODIFIED NEWTON-RAPHSON METHOD
      DD(1)=1.0+FK1*(FFK*(2.0*A1+B2)+A1*(A1+B2))*HH2S/FFK**2
      PH2S=PHS-F1/DD(1)
      A1=MM*XH2S-HH2S*PH2S
      FFK=MM-Z-A1-B2
      IF(FFK)955,955,956
955   FFK=MM/50.0
956   F2=PCO2-FK2*Z*(A1+B2)/FFK**2
      DD(2)=1.0+FK2*Z*HCO2*(FFK**2+2.0*FFK*(A1+B2))/FFK**4
      PCO2=PCO-F2/DD(2)
      B2=MM*XCO2-HCO2*PCO2
      FFK=MM-Z-A1-B2
      IF(FFK)957,957,958
957   FFK=MM/50.0
958   DD(3)=1.0+FK3*(FFK+B2-Z)
525   F3=Z-FK3*(B2-Z)*FFK
      Z=ZZ-F3/DD(3)
      IF(Z)505,505,506
```

```
  505 ZZ=2.0*ZZ
      GO TO 525
  506 IF((XCO2+XH2S)-0.2)833,833,934
  934 DHL=ALOG(ALPHA)/2.303+8.65-0.2150E04/T
      PH2O=EXP(2.303*DHL)
      P=PH2S+PCO2+PH2O
      PP=P/51.70
      IF(PP-50.0)933,935,935
  935 Y(1)=PH2S/P
      Y(2)=PCO2/P
      Y(3)=PH2O/P
      TRT=(T-273.16)*1.8+492.0
      CALL FUGCF(PP,TRT,Y,PHI)
      PH2S=PH2S/PHI(1)
      PCO2=PCO2/PHI(2)
      GO TO 933
  833 PPH=PH2S*(1.0-EXP(-XH2S*0.01)+2.0*EXP(-(0.06/XH2S))+EX
     1P(-0.05/(XCO2+XH2S*1.0)))*(1.0-0.00009/(XH2S**2))*(1.0
     2+(XCO2**2)/(2.5*XH2S))
      PH2S=PPH
      PPC=PCO2*(1.0-EXP(-XCO2*0.01)+2.0*EXP(-(0.07/XCO2))+EX
     1P(-0.05/(XCO2*0.2+XH2S)))*(1.0-0.002/XH2S)*(1.0-0.004/
     2XCO2)*(1.0+XH2S**2/(1.5*XCO2))
      PCO2=PPC
C     CHECKING OF CORRECTED VALUES
  933 IF(ABS((PH2S-PHS)/PH2S*100.0)-5.0)14,19,19
  14  IF(ABS((PCO2-PCO)/PCO2*100.0)-1.0)16,19,19
  16  IF(ABS((Z-ZZ)/Z*100.0)-5.0)69,19,19
  19  PHS=PH2S
      PCO=PCO2
      ZZ=Z
      IF(KL-11)40,40,405
  405 WRITE(6,406)
  406 FORMAT(//,15X,'NO CONVERGENCE AFTER 11 ITERATIONS' //,
     110X,'THE LAST ESTIMATES WERE AS FOLLOWS :',//)
      WRITE(6,100)XCO2,XH2S,Z,PCO2,PH2S
      GO TO 108
  69  WRITE(6,400)AA,ALPHA
  400 FORMAT(//,2X,'AA=',F7.4,//,2X,'ALPHA=',F7.4)
      WRITE(6,77)KL
  77  FORMAT(//,2X,'NO. OF ITERATIONS FOR CONVERGENCE TO PAR
     1TIAL PRESSURES=',I3)
      PH2S=PH2S/51.7
      PCO2=PCO2/51.7
      WRITE(6,100)XCO2,XH2S,Z,PCO2,PH2S
  100 FORMAT(//,9X,'XCO2',13X,'XH2S',10X,'RNHCOO(-)',6X,
     1'CO2 PARTIAL PRESS.',4X,'H2S PARTIAL PRESS.',//,2X,5E16.5,/
  108 CONTINUE
      CALL EXIT
      END
```

```
 **************************************************************
 *                                                            *
 * SUBROUTINE FUGCF CALCULATES THE FUGACITY COEFFICIENTS      *
 *  OF CARBON-DIOXIDE AND HYDROGEN-SULPHIDE                   *
 *                                                            *
 *  VALUES IN THE CALLING SEQUENCE ARE ,                      *
 *  P - TOTAL PRESSURE IN PSIA                                *
 *  T - TEMPERATURE IN DEGREES RANKINE                        *
 * Y - MOLE FRACTIONS OF H2S,CO2 AND WATER RESPECTIVELY       *
 *  PHI - INITIAL FUG. COEFF. VECTOR                          *
 *                                                            *
 **************************************************************
      SUBROUTINE  FUGCF (P,T,Y,PHI)
      DIMENSION Y(3)
      DIMENSION AIRKV(3),A(4),Z(3)
      DIMENSION PHILN(3),PHI(3)
      DIMENSION ARKV(3,3),BRKV(3),PCIJV(3,3),TCIJV(3,3)
      DIMENSION GA(3),GB(3),PC(3),TC(3),VC(3)
      DATA GA/0.4340,0.4470,0.421/
      DATA GB/0.0882,0.0911,0.08368/
      DATA TC/672.7,240.0,1165.6/
      DATA VC/1.5606,2.3408,0.90/
      DATA PC/1306.0,1071.0,3208.0/
      PCIJV(1,2)=0.5741E03
      PCIJV(1,3)=0.21615E04
      PCIJV(2,3)=0.10825E04
      TCIJV(1,2)=0.3697E03
      TCIJV(1,3)=0.8855E03
      TCIJV(2,3)=0.5289E03
      R=10.73
      DO 200 I=1,3
      BRKV(I)=GB(I)*R*TC(I)/PC(I)
      ARKV(I,I)=GA(I)*R**2*TC(I)**2.5/PC(I)
      DO 200 J=1,3
      PCIJV(J,I)=PCIJV(I,J)
      TCIJV(J,I)=TCIJV(I,J)
      IF(I-J)2,200,2
  2   ARKV(I,J)=((GA(I)+GA(J))*R**2*TCIJV(I,J)**2.5)/(2.0*PCIJV(I
  200 CONTINUE
C     CALCULATION OF AMRKV,BRMKV
      AMRKV=0.0
      BMRKV=0.0
      DO 120 I=1,3
      AIRKV(I)=0.0
      BMRKV=BMRKV+Y(I)*BRKV(I)
      DO 120 J=1,3
      AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
  120 AMRKV=AMRKV+Y(I)*Y(J)*ARKV(I,J)
C     CALCULATION OF VAPOR MOLAR VOLUME OF MIXTURE
      A(1)=1.0
      A(2)=-1.0
      PBRT=P*BMRKV/(R*T)
      ABRT=AMRKV/(BMRKV*10.73*T**1.5)
      A(3)=PBRT*(ABRT-1.0-PBRT)
      A(4)=-ABRT*PBRT**2
      Z(1)=0.0
      Z(2)=0.0
      Z(3)=0.0
      MTYPE=-1
      CALL CUBEQ(A,MTYPE,Z)
      IF(MTYPE)130,140,140
  130 ZV=AMAX1(Z(1),Z(2),Z(3))
      GO TO 150
  140 ZV=Z(1)
  150 VV=ZV*R*T/P
C     FUGACITY COEFFICIENTS WITH MODIFIED R-K EQN.
      QVVB=ALOG(VV/(VV-BMRKV))
      Q1VB=1.0/(VV-BMRKV)
      Q2RTB=2.0/(10.73*T**1.5*BMRKV)
      QVBV=ALOG((VV+BMRKV)/VV)
      QARTB=AMRKV/(10.73*T**1.5*BMRKV**2)
      QBVB=BMRKV/(VV+BMRKV)
      DO 160 I=1,3
      PHILN(I)=QVVB+BRKV(I)*Q1VB-AIRKV(I)*Q2RTB*QVBV+BRKV(I)*QART
     1-QBVB)-ALOG(ZV)
      PHI(I)=EXP(PHILN(I))
  160 CONTINUE
      RETURN
      END
```

```
*************************************************************
*                                                           *
*  SUBROUTINE AMAX1 FINDS THE MAX. Z VALUE                  *
*                                                           *
*************************************************************
      FUNCTION AMAX1(RR,SS,UU)
      AMAX1=RR
      IF(AMAX1-SS)2,3,3
  2   AMAX1=SS
  3   IF(AMAX1-UU)4,5,5
  4   AMAX1=UU
  5   RETURN
      END
```

```
************************************************************
*                                                          *
*  THIS SUBROUTINE SOLVES CUBIC REDLICH-KWONG EQUATION     *
*  FOR COMPRESSIBILITY FACTORS                             *
*                                                          *
************************************************************
      SUBROUTINE  CUBEQ (A,MTYPE,Z)
      DIMENSION B(3),A(4),Z(3)
C
      B(1) = A(2)/A(1)
      B10V3 = B(1)/3.0
      B(2) = A(3)/A(1)
      B(3) = A(4)/A(1)
      ALF = B(2) - B(1)*B10V3
      BET = 2.0*B10V3**3 - B(2)*B10V3 + B(3)
      BETOV  = BET/2.0
      ALFOV  = ALF/3.0
      CUAOV  = ALFOV **3
      SQBOV  = BETOV **2
      DEL = SQBOV  + CUAOV
      IF (DEL) 40,20,30
   20 MTYPE = 0
      GAM = SQRT (-ALFOV )
      IF (BET) 22,22,21
   21 Z(1) = -2.0*GAM -B10V3
      Z(2) = GAM -B10V3
      Z(3) = Z(2)
      GO TO 50
   22 Z(1) = 2.0*GAM -B10V3
      Z(2) = -GAM -B10V3
      Z(3) = Z(2)
      GO TO 50
   30 MTYPE = 1
      EPS = SQRT (DEL)
      TAU = -BETOV
      RCU=TAU+EPS
      SCU=TAU-EPS
      SIR=1.0
      SIS=1.0
      IF (RCU) 31,32,32
   31 SIR=-1.0
   32 IF (SCU) 33,34,34
   33 SIS=-1.0
   34 R=SIR*(SIR*RCU)**0.33333333
      S=SIS*(SIS*SCU)**0.33333333
      Z(1) = R + S - B10V3
      Z(2) = -(R+S)/2.0 * B10V3
      Z(3) = 0.86602540*(R-S)
      GO TO 50
   40 MTYPE = -1
      QUOT = SQBOV /CUAOV
      ROOT = SQRT (-QUOT)
   IF(BET) 42,41,41
41 PEI = (1.5707963 + ATAN (ROOT / SQRT (1.0 - ROOT**2))) / 3.
   GO TO 43
42 PEI = ATAN (SQRT (1.0 - ROOT**2) / ROOT) / 3.0
43 FACT = 2.0*SQRT (-ALFOV )
   Z(1) = FACT*COS (PEI) - B10V3
   PEI=PEI+2.0943951
   Z(2) = FACT*COS (PEI) - B10V3
   PEI=PEI+2.0943951
   Z(3) = FACT*COS (PEI) - B10V3
50 CONTINUE
   RETURN
   END
```

APPENDIX G

EMPIRICAL CORRECTION FACTORS FOR MODIFIED KLYAMER ET AL. MODEL.

CORRECTED GAMA FUNCTIONS WHEN XCO2+XH2S IS >0.20

(1) FOR MEA

```
 GAMA=0.399117-0.338402E-02*MU+0.324219E00*EXP(-MU)+0.1
15*(1.0-(0.21/(XCO2+XH2S))**0.95)+((XCO2+XH2S-0.4)/(1.0
2+EXP(-(7.2-MM))))*(1.1-EXP(-(374.0-T)/100.0))
```

(2) FOR DEA

(I) WHEN ONLY ONE ACID GAS IS PRESENT

```
 GAMA=0.36640-0.15975E-01*MU+0.344379E00*EXP(-MU)+(0.10
10*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.1*((XCO2+XH2S-0.05)
2/(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0)))*(1.05-EXP(
3-(5.22-MM)/10.0))
```

(II) FOR MIXTURES OF H2S AND CO2

```
 GAMA=0.36640-0.15975E-01*MU+0.344379E00*EXP(-MU)+(0.10
1*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.5*((XCO2+XH2S-0.30)/
2(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0)))
```

CORRECTED PARTIAL PRESS. FUNCTIONS FOR XCO2+XH2S<0.20

```
 PPH=PH2S*(1.0-EXP(-XH2S*0.01)+2.0*EXP(-(0.06/XH2S))+EX
1P(-0.05/(XCO2+XH2S*1.0)))*(1.0-0.00009/(XH2S**2))*(1.0
2+(XCO2**2)/(2.5*XH2S))

 PPC=PCO2*(1.0-EXP(-XCO2*0.01)+2.0*EXP(-(0.07/XCO2))+EX
1P(-0.05/(XCO2*0.2+XH2S)))*(1.0-0.002/XH2S)*(1.0-0.004/
2XCO2)*(1.0+XH2S**2/(1.5*XCO2))
```

APPENDIX H

POLYNOMIAL APPROXIMATIONS OF K_i, K_w, K_{1C}, K_{2C}, H_{H_2S}, K_m, K_{1Y}, K_{2Y}, H_{CO_2}, γ and a

$$k_i \text{ (DEA)} = \frac{K_w \times 10^8}{e^{-1.609 + 0.0415(T - 37.8)}} \qquad T = °C$$

For MEA

If T < 65° $K_m = e^{4.58 \times 10^3(1/T-0.00295)-1.5}$ $T = °K$

If T > 65°C $K_m = e^{4.742 \times 10^3(1/T-0.0025)-3.634}$ $T = °K$

For DEA

$$Km = e^{3.66 \times 10^3(1/T-0.0026)-4.0} \qquad T = °K$$

$$Y_1 = a_o + a_1x + a_2x^2 + a_3x^2$$

$$Y_2 = a_o + a_1x + a_2e^{-x}$$

$$Y_3 = a_o/x + a_1 + a_2x$$

Y_i	x	a_o	a_1	a_2	a_3
$K_{1Y} = e^{Y_1}$	1/T (K^{-1})	8.724	-1.833	0.3375	-
$H_{H_2S} = e^{Y_1}$	T (°K)	-4.508	0.0453	-6×10^{-5}	-
$H_{CO_2} = e^{Y_1}$	T (°K)	-2.4835	0.03612	4.4×10^{-5}	-
$K_w = e^{Y_1}$	T (°F)	-0.7564	0.0279	7.0×10^{-5}	7.47×10^{-8}
$K_{1C} = e^{Y_1}$	T (°F)	0.1108	0.0167	6.85×10^{-5}	1.07×10^{-7}
$a(DEA) = Y_1$	m(molality)	0.8575	1.258×10^{-2}	4.42×10^{-3}	-
$a(MEA) = Y_1$	$m \geq 0.4$	0.8727	-	-	-
$\gamma = Y_2$	$\mu \leq 0.1$	0.9623	-1.996	-0.068	-
$\gamma(MEA) = Y_2$	$\mu > 0.1$	0.3991	-3.384×10^{-3}	0.3242	-
$\gamma(DEA) = Y_2$	$\mu > 0.1$	0.3664	1.598×10^{-2}	0.3444	-
$K_1(MEA) = \frac{K_w}{e^{2.303\,Y_3}}$	T (°K)	-2677.9	-0.6169	4.277×10^{-4}	-